



Terhi Hirvikorpi

Thin Al_2O_3 barrier coatings grown on bio-based packaging materials by atomic layer deposition

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Terhi Hirvikorpi

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Terhi Hirvikorpi. Thin Al₂O₃ barrier coatings grown on bio-based packaging materials by atomic layer deposition [Ohuet biopohjaisille pakkausmateriaaleille atomikerroskasvatetut Al₂O₃-barrier-pinnoitteet]. Espoo 2011. VTT Publications 770. 74 p. + app. 42 p.

Keywords: atomic layer deposition, aluminium oxide, thin film, barrier, biopolymer, packaging material

Abstract

Growing environmental concerns related to the use of synthetic non-biodegradable polymers in the packaging industry have led to the need for new, especially bio-based, materials. Currently, petroleum-based synthetic polymers are widely used due to their relatively low cost and high performance. Biodegradable plastics and fibre-based materials have been proposed as a solution to the waste problems related to these synthetic polymers. Fibre-based packaging materials have many advantages over their non-biodegradable competitors, such as stiffness vs. weight ratio and recyclability. However, poor barrier properties and sensitivity to moisture are the main challenges restricting their use. Application of a thin coating layer is one way to overcome these problems and to improve the barrier properties of such materials.

Atomic layer deposition (ALD) is a well suited technique for depositing thin inorganic coatings onto temperature-sensitive materials such as polymer-coated boards and papers and polymer films. In the present work, thin and highly uniform Al₂O₃ coatings were deposited at relatively low temperatures of 80, 100 and 130 °C onto various bio-based polymeric materials employing the ALD technique. The study demonstrates that a 25-nm-thick ALD-grown Al₂O₃ coating significantly enhances the oxygen and water vapour barrier performance of these materials. Promising barrier properties were obtained with polylactide-coated board, hemicellulose-coated board as well as various biopolymer (polylactide, pectin and nanofibrillated cellulose) films after coating with a 25-nm-thick Al₂O₃ layer.

Thin Al₂O₃ coatings can improve the properties of biopolymers, enabling the use of these renewable polymers in the production of high-performance materials for demanding food and pharmaceutical packaging applications. The future roll-to-roll ALD technology for coating polymers with inorganic thin films will increase the industrial potential of these materials and could lead to further opportunities for their commercialization.

Terhi Hirvikorpi. Thin Al_2O_3 barrier coatings grown on bio-based packaging materials by atomic layer deposition [Ohuet biopohjaisille pakkausmateriaaleille atomikerroskasvatetut Al_2O_3 -barrier-pinnoitteet]. Espoo 2011. VTT Publications 770. 74 p. + app. 42 p.

Avainsanat: atomic layer deposition, aluminium oxide, thin film, barrier, biopolymer, packaging material

Tiivistelmä

Pakkausteollisuuden tietoisuus synteettisten biohajoamattomien muovien ympäristöhaitoista on lisännyt tarvetta ekologisemmille biopohjaisille pakkausratkaisuille. Nykyisin öljypohjaisia synteettisiä polymeerejä käytetään useissa pakkauksissa, koska ne ovat halpoja ja ominaisuuksiltaan hyviä. Biohajoavia muovi- ja kuitupohjaisia materiaaleja pidetään ratkaisuna öljypohjaisten synteettisten muovien aiheuttamalle jäteongelmalle. Kuitupohjaisilla pakkausmateriaaleilla on monia hyviä ominaisuuksia verrattuna niiden biohajoamattomiin kilpailijoihin, kuten painoon suhteutettu kestävyys ja kierrätettävyys. Niiden heikkoutena on kuitenkin huono kosteuden sietokyky sekä korkea vesihöyrynläpäisy, jotka estävät tuotteiden laajamittaisen käytön. Materiaalien läpäisynestoa voidaan parantaa sopivilla pinnoituksilla.

Atomikerroskasvatus ohutpinnoitteiden valmistustekniikkana soveltuu hyvin epäorgaanisten pinnoitteiden kasvatukseen lämpöherkille materiaaleille, jollaisia esimerkiksi polymeeripinnoitetut kartongit ja paperit sekä polymeerikalvot ovat. Tässä työssä kasvatettiin ohuita Al_2O_3 -kalvoja suhteellisen alhaisissa lämpötiloissa (80, 100 ja 130 °C:ssa) ALD-tekniikalla monenlaisille biopohjaisille polymeerisubstraateille. Ohuet (25 nm) ALD-tekniikalla valmistetut Al_2O_3 -pinnoitteet mahdollistavat huomattavan parannuksen biopohjaisten pakkausmateriaalien hapen- ja vesihöyrynläpäisyn estokykyyn. Polylaktidilla ja hemiselluloosalla päällystetyt kartongit sekä polylaktidista, pektiinistä ja nanoselluloosasta valmistetut kalvot olivat lupaavia hapen ja vesihöyrynläpäisyä estäviä materiaaleja, kun ne oli päällystetty 25 nm:n paksuisella Al_2O_3 -kerroksella.

Nämä ohuet pinnoitteet aikaansaavat niin merkittävän parannuksen esto-ominaisuuksissa, että biopolymeerien käyttö vaativissakin pakkaussovelluksissa, kuten elintarvike- ja lääkepakkauksissa, mahdollistuu. ALD-teknologian kehitys kohti rullalta rullalle -prosessia mahdollistaa epäorgaanisten pinnoitteiden valmistamisen teollisessa mittakaavassa, mikä on elintärkeää tässä työssä esiteltujen uusien pakkausmateriaalien kaupallistumiselle.

Academic dissertation

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*Kuka vain, minä vain, sinä vain
Kaiken avain, voit muuttaa suuntaa*

Teräsbetoni,
Maailma tarvitsee sankareita

Preface

The experimental work for this thesis was carried out at Oy Keskuslaboratorio – Centrallaboratorium Ab (KCL) and at VTT Technical Research Centre of Finland between November 2007 and December 2010.

I would like to express my sincere gratitude to my supervisor Academy Prof. Maarit Karppinen of the Laboratory of Inorganic Chemistry at the Aalto University School of Chemical Technology for investing such enormous time and effort in guiding this work. I also extend my appreciation to my instructors at VTT, Dr. Mika Vähä-Nissi and Prof. Ali Harlin, for their valuable guidance and for the opportunity to work on this subject, which is close to my heart. My sincere thanks go also to the pre-examiners of this thesis for their work and helpful advice. I am deeply thankful to my co-workers and friends at VTT and especially to Ms. Jenni Sievänen, Ms. Hanna Heinonen, Dr. Riku Talja and Dr. John Kettle for bringing laughter and joy to work and always being there for me.

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Espoo, September 2011

Terhi Hirvikorpi

List of publications

The thesis consists of an introductory summary and the six publications listed below. The publications are referred to in the text by the roman numerals I–VI.

- I** T. Hirvikorpi, M. Vähä-Nissi, A. Harlin and M. Karppinen, Comparison of some coating techniques to fabricate barrier layers on packaging materials, *Thin Solid Films* **518** (2010) 5463–5466.
- II** T. Hirvikorpi, M. Vähä-Nissi, T. Mustonen, E. Iiskola and M. Karppinen, Atomic layer deposited aluminum oxide barrier coatings for packaging materials, *Thin Solid Films* **518** (2010) 2654–2658.
- III** T. Hirvikorpi, M. Vähä-Nissi, J. Nikkola, A. Harlin and M. Karppinen, Thin Al_2O_3 barrier coatings onto temperature-sensitive packaging materials by atomic layer deposition, *Surface and Coatings Technology*, **205** (2011) 5088–5092.
- IV** T. Hirvikorpi, M. Vähä-Nissi, A. Harlin, J. Marles, V. Miikkulainen and M. Karppinen, Effect of corona pre-treatment on the performance of gas barrier layers applied by the atomic layer deposition onto polymer-coated paperboard, *Applied Surface Science* **257** (2010) 736–740.
- V** T. Hirvikorpi, M. Vähä-Nissi, J. Vartiainen, P. Penttilä, J. Nikkola, A. Harlin, R. Serimaa and M. Karppinen, Effect of heat-treatment on the performance of gas barrier layers applied by atomic layer deposition onto polymer-coated paperboard, *Journal of Applied Polymer Science* **122** (2011) 2221–2227.
- VI** T. Hirvikorpi, M. Vähä-Nissi, A. Harlin, M. Salomäki, S. Areva, J.T. Korhonen and M. Karppinen, Enhanced water vapor barrier properties for biopolymer film by polyelectrolyte multilayer and atomic layer deposited Al_2O_3 double-coating, *Applied Surface Science* **257** (2011) 9451–9454.

Contributions of the author

- I** Designed the experiments, carried out the thickness measurements, supervised the characterizations (ICP-AES, AFM, OTR and WVTR), evaluated all of the results and had a major role in writing the manuscript.
- II** Designed the experiments, carried out the TG analyses, supervised the characterizations (SEM, AFM, OTR and WVTR), evaluated all of the results and had a major role in writing the manuscript.
- III** Designed the experiments, carried out the ALD coatings and some of the CA, SE and OTR measurements, supervised the CA, SE, OTR and WVTR measurements, evaluated all of the results and had a major role in writing the manuscript.
- IV** Designed the experiments, carried out the corona treatments and CA and SE analyses, supervised the OTR and WVTR measurements, evaluated all of the results and had a major role in writing the manuscript.
- V** Designed the experiments, carried out the ALD coatings, some of the thermal treatments and the CA and SE analyses, supervised the characterizations (AFM, OTR and WVTR) evaluated all of the results and had a major role in writing the manuscript.
- VI** Designed the experiments, carried out the fabrication of the PE solutions, PEM coatings on silicon wafer and characterizations (thickness, M_v , cytotoxicity and CA), supervised the fabrication of PEM coatings on PLA and characterizations (SEM and WVTR), evaluated all of the results and had a major role in writing the manuscript.

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List of abbreviations

AFM	Atomic force microscopy
ALD	Atomic layer deposition
ALG	Sodium alginate
B	Board
BfR	Bundesinstitut für risikobewertung (German federal institute for risk assessment)
CA	Contact angle (°)
CHI	Chitosan
CVD	Chemical vapour deposition
DIM	Diiodomethane
EBE	Electron beam evaporation
EDS	Energy dispersive spectroscopy
EVOH	Ethylene vinyl alcohol
FDA	Food and drug administration
GGM	Galactoglucomannan
GPC	Growth per cycle
ICP-AES	Inductively-coupled plasma atomic emission spectroscopy
LbL	Layer-by-layer
LDPE	Low-density polyethylene
MLD	Molecular layer deposition

MS	Magnetron sputtering
NFC	Nanofibrillated cellulose
OTR	Oxygen transmission rate ($\text{cm}^3/\text{m}^2/10^5 \text{ Pa/day}$)
OWRK	Extended Fowkes theory
PC	Polycarbonate
PE	Polyethylene
PECVD	Plasma-enhanced chemical vapour deposition
PEM	Polyelectrolyte multilayer film
PEN	Polyethylene naphthalene
PET	Polyethylene terephthalate
PHB	Polyhydroxybutyrate
PLA	Poly lactide
PMMA	Polymethyl methacrylate
PP	Polypropylene
PS	Polystyrene
PVC	Polyvinyl chloride
PVD	Physical vapour deposition
R _a	Average roughness (m)
RH	Relative humidity (%)
RT	Room temperature
SCCM	Standard cubic centimetres per minute
SEM	Scanning electron microscopy
SG	Sol-gel
TG	Thermogravimetry
TMA	Trimethylaluminium

UNC	Uncoated
WAXS	Wide-angle X-ray scattering
WVTR	Water vapour transmission rate (g/m ² /day)
XPS	X-ray photoelectron spectroscopy

List of symbols

A	Effective area of permeation (m^2)
a	Mark–Houwink parameter (-)
c	Concentration of the permeant molecule (mol/l)
D	Diffusion coefficient (m^2/s)
E_d	Activation energy of diffusion (kJ/mol)
F	Diffusing rate per unit of area ($\text{g/m}^2\text{s}$)
k	Boltzmann constant ($1.380650 \cdot 10^{-23} \text{ JK}^{-1}$)
K	Mark–Houwink parameter (ml/g)
l	Thickness of the packaging material (m)
M_v	Molecular weight (g/mol)
P	Permeability coefficient (g/msPa)
q	Quantity of permeant molecule (volume or mass) passing through the packaging material (m^3 or kg)
S	Solubility coefficient ($\text{g}/(\text{m}^3\text{Pa})$)
t	Evaluation time (s)
T	Temperature (K)
x	Direction of diffusion (-)
$[\eta]_{in}$	Intrinsic viscosity (ml/g)
Δp	Pressure difference between both sides of the packaging material (Pa)
γ_s	Total surface energy (mN/m)
γ^d	Dispersive component of surface energy (mN/m)
γ^p	Polarity component of surface energy (mN/m)

1. Introduction

Synthetic non-biodegradable polymers derived from petroleum-based resources, such as polyethylene, polypropylene, polyethylene terephthalate, etc., are widely used materials in food and pharmaceutical packaging applications due to their relatively low cost and high performance. However, growing environmental concerns related to the use of these polymers has led to the need for new solutions, and biopolymers (modified natural polymers, and biodegradable synthetic polymers of bio-based monomers) have been considered to be the environmentally-friendly solution for packaging materials in the future [1]. In many cases, however, poor barrier properties, especially of natural polymers, and sensitivity to moisture are preventing the wider use of these materials. In order to commercialize novel materials from renewable sources, the properties of these materials must be improved to a level that matches or exceeds the properties of the materials currently in use without sacrificing recyclability. One way to improve the barrier properties of biopolymers is to coat them with a thin inorganic layer.

Atomic layer deposition (ALD) is an advanced thin-film deposition technique that enables the production of high-quality coatings on a range of materials [2,3]. The technique's layer-by-layer growth assures precise control of film thickness even at relatively low process temperatures. Similar process control, mild deposition conditions and high film quality combined with low thickness is difficult to obtain with other thin-film deposition techniques. The goal of the present work was to deposit ultra-thin high-quality barrier coatings onto polymeric materials. The emphasis was on biopolymeric materials, such as polylactide (PLA). The ALD-grown Al_2O_3 coatings were shown to produce significantly enhanced oxygen and water vapour barrier materials when coated onto temperature-sensitive biopolymeric materials.

Nowadays biopolymers are used in relatively few packaging products. Thin (25 nm or less) Al_2O_3 coatings can extend the use of these polymers towards more demanding packaging applications such as dry food and pharmaceutical packages. The fabrication of recyclable and biodegradable barrier materials represents a new approach to utilizing the ALD technique. The results led to optimization of the ALD process parameters (most suitable oxygen source, deposition temperature, and film thickness) for biopolymeric materials. In addition, the effects on barrier properties of various pre-treatments and pre-coatings carried out prior to the ALD process were studied.

Numerous non-biodegradable and bio-based polymers have been developed as commercial barrier materials by companies and research institutes. The polymers currently in use are presented in Chapter 2. ALD coatings offer the potential to raise the properties of these materials to new, improved levels. However, due to the highly complex nature of the barrier phenomena involved, this goal is not easy to achieve. The gas barrier phenomena in question are briefly presented in Chapter 3. In addition to a description of the ALD process, the currently used thin-film deposition techniques related to the packaging industry are discussed in Chapter 4.

The experimental section, including a description of the substrate materials and the characterization techniques employed during the work, is presented in Chapter 5. The main characterization methods utilized were the barrier testing methods, i.e. oxygen and water vapour transmission rates (OTR, WVTR). The oxygen and water vapour barrier properties of temperature-sensitive bio-based materials combined with ALD-grown Al_2O_3 coatings have not been as extensively studied before. Chapter 5 also describes the methods applied to improve the barrier properties of the polymeric materials prior to the ALD process. Chapters 6 and 7 summarize the results. Chapter 7 also describes the current development status of these materials and provides recommendations for future research.

The future of the materials studied here looks bright. The future use of roll-to-roll ALD technology to produce inorganic coatings on polymers will increase the industrial potential of these materials as the process becomes more cost-effective [4]. This development is being supported by new competence and research tools and evidenced by new inventions and patent applications [5–7]. Process development is also essential for the commercialization of these novel packaging materials, which is predicted to be a reality within the next few years.

2. Polymeric packaging materials

2.1 The use of biopolymers as packaging materials

The use of polymers from renewable sources, i.e. biopolymers, as a replacement for synthetic non-biodegradable polymers as packaging materials is believed to offer a future means of significantly reducing non-compostable packaging waste and mitigating the greenhouse effect [8]. The use of biopolymers as packaging materials is increasing due to their advantageous properties. For instance, in many cases they are completely biodegradable within the composting cycle. Due to similar properties with petroleum-based polymers, biopolymers, such as polylactide (PLA) can be used to replace conventional polymers, such as polystyrene (PS) or polypropylene (PP). In addition, biopolymers can be fabricated from renewable biomass which will not eventually run out as will the feedstock of petrochemicals making biopolymers a sustainable alternative for the packaging industry. However, when compared to synthetic thermoplastic polymers such as polypropylene or polyethylene, the use of biopolymers is limited due to their naturally poor moisture barrier properties. The recyclable packaging materials currently on the market are mainly based on starch or PLA. In the packaging industry, biopolymers are used in applications such as biodegradable waste bags, fast food service-ware, and food containers.

Biopolymers are classified according to their source of extraction or the production method used [9]. Biopolymers are referred to as natural polymers if they have been extracted or removed from biomass [10,11]. Natural polymers are formed during the natural growth processes of organisms. Biopolymers can be produced by classical chemical synthesis starting from renewable bio-based monomers, or they can be produced by micro-organisms. Thermoplastic, biodegradable PLA is a biopolymer produced by polymerization of lactic acid monomers or cyclic lactide dimers [12]. Biodegradable polymers of fossil origin

also exist, such as polycaprolactone, although these cannot be defined as biopolymers.

The diversity of packed food and pharmaceutical goods will increase in the future, as will the requirement for more sustainable packaging materials [12]. Fibre-based materials refer to materials made from cellulosic fibre networks, such as paper and board. Paper and board products must compete with plastics for market share. Paper and board base materials are often coated with polymers or treated in some other way to enhance their mechanical and barrier properties. Fibre-based materials have advantages and disadvantages similar to biopolymers [13]. These materials are often compostable within the composting cycle but their moisture resistance is poor. In addition, their stiffness vs. weight ratio is also excellent and hard to beat. Due to problems in the recycling process posed by synthetic non-biodegradable polymers, novel, easily recyclable, fibre-based materials have been developed for these applications [1,14].

Polymer waste can be managed in three ways: mechanical recycling, energy recovery, or biological recycling [14]. Additionally, monomer recycling has also been proposed for several polymers such as polyvinyl chloride, although the concept has not proven feasible to date. Mechanical recycling is the most beneficial approach in cases where the recycled polymer only partially replaces the polymer in the primary product. The main obstacle in the recycling process is thermal decomposition of the polymer. In addition, polymers often contain impurities after recycling. Energy recovery from polymers is potentially a beneficial option, as petroleum-based polymers contain large amounts of energy and could be used as a partial replacement for fossil fuels. However, the formation of toxic gases during the incineration of polymers remains a key problem in this respect. Biological recycling refers to the composting of organic matter, i.e. the returning of polymers to biomass. Biological recycling is the most beneficial method where mechanical recycling and energy recovery are inefficient, for example in the case of food packages containing food waste.

2.2 The selection of suitable packaging materials

The choice of packaging material for a given application depends on a range of factors. The type of packed good, its chemical composition, size, storage conditions, expected shelf life, moisture content, aromas and appearance are just a few characteristics to be considered in the material selection. The chosen material must protect both the packed item and the environment. In the case of

food and pharmaceutical packages, health and hygiene must also be accounted for. The approved packaging materials for food and pharmaceutical products are restricted by law. In the USA, the Food and Drug Administration (FDA) regulates factors affecting migration and changes in odour and flavour. In Europe, one major regulator is the German Federal Institute for Risk Assessment (Bundesinstitut für Risikobewertung, BfR) [15–17]. In addition, the European Union and its legislation on packaging and packaging waste regulate the suitability of packaging materials in Europe.

In order to provide sufficient protection the packaging material must be multifunctional, as it must serve as a barrier against gases, moisture, light, grease and aromas. In addition, it must be durable and sealable. This must also be achieved at low production cost and with low energy consumption [18]. Polyethylene (PE) as a commercial synthetic petroleum-based polymer is a poor oxygen barrier, but has good water and water vapour barrier properties. Besides low- and high-density PE, the common non-biodegradable moisture barrier polymers include PP and polyethylene terephthalate (PET) [19,20]. Other similar polymers with moisture barrier properties include cyclo-olefin copolymers, liquid-crystal polymers and nano-composites [21,22]. In addition, vinyl alcohol polymers, such as ethylene vinyl alcohol (EVOH) are examples of petroleum-based polymers that have good oxygen, but poor water vapour barrier properties due to their polar groups, which cause them to be hydrophilic [1]. Hygroscopic materials, such as many biopolymers (especially polymers from natural sources), typically lose their barrier properties at high relative humidity [23]. This is mainly due to the adsorption of moisture from the environment by the biopolymer which causes the polymer structure to swell, resulting in a more porous structure. Although PLA lacks high oxygen and moisture barrier properties as such, it has potential due to the fact that it is recyclable and fulfils the requirements for direct contact with aqueous, acidic and fatty foods [24].

Often single polymer lacks sufficient barrier properties for demanding applications. Multilayer structures are employed as a means of improving barrier performance by combining the desirable barrier properties of individual materials [25]. Traditionally, multilayer structures incorporating aluminium foil and polymer films or metallized aluminium films have been used as barriers for gases, moisture and light [19,20]. However, the key drawback of aluminium foil is its lack of recyclability. The development of replacements for aluminium foil has therefore gained considerable attention, and improved water vapour and oxygen barrier properties for polymers have been achieved using thin SiO_x coatings [21,26].

3. Permeation through polymeric materials

3.1 Mass transfer interactions

In a polymeric packaging system, numerous interactions take place between the packed items and the packaging material. The internal and external environments of a package have different concentrations of specific compounds [27]. The fundamental driving force behind the interactions is chemical potential, which causes molecules to diffuse into and through the packaging material. These molecules tend naturally to move from the side of higher concentration to that of lower concentration. The interactions can be classified into three groups: mass transfer, biological exchange, and energy exchange interactions. This chapter focuses exclusively on mass transfer interactions, as these have the biggest influence on gas and water vapour barrier properties during the shelf-life of a packaged product [27]. Shelf-life refers to the time from fabrication to opening of the package. The mass transfer phenomena are illustrated in Figure 1.

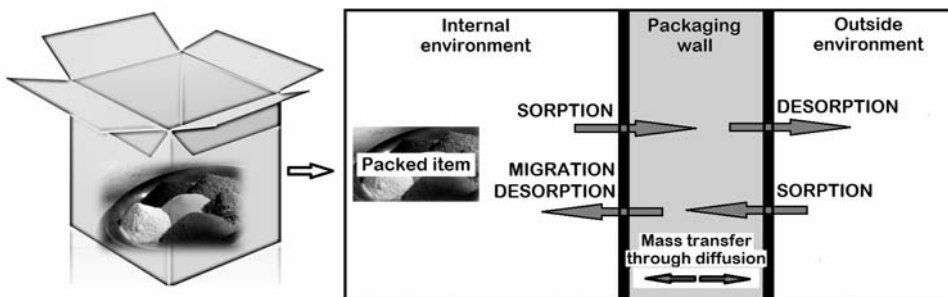


Figure 1. Mass transfer processes through and from a polymeric packaging wall (modified from Hernandez et al. [27]).

3. Permeation through polymeric materials

Mass transfer processes involve the process of permeation. Permeation refers to the movement of molecules between the packed item and the outside environment. Permeation is a complex process which involves sorption of the permeant into the polymer from the high concentration side, diffusion through the material, and desorption from the polymer on the low concentration side. Transfer of permeants between the packaging material and the immediate environment or product includes sorption, desorption and migration. The molecules move to the packaging wall by sorption and out of the packaging wall to the outside environment by desorption. Sorption also describes the dissolution of the permeant molecules at the packaging wall surface prior to diffusing through the wall. Migration refers to the release of migrating species directly from the packaging material into the packed item. In such a case, the packed item must be in direct contact with the packaging wall. In cases where the packaging wall is in contact with the protecting gas, i.e. the protecting atmosphere in the package, the molecules move by desorption from the packaging wall into the gas. Migrating species typically consist of small residues of monomer from the polymerization process, plasticizers or other additives [15], but may also include chemicals from the packaging board, printing inks or the package's sealing adhesives [28,29]. Migration is controlled by diffusion and driven by concentration gradients. If the packed item comes into contact with the packaging material, species may migrate causing possible health risks.

Permeants consist of low molecular weight molecules such as aromatic compounds, oxygen (O₂), carbon dioxide (CO₂) and water (H₂O). The degree of permeation of these molecules through a specific packaging material can be described by the permeability coefficient (P) of the material. Diffusion, solubility and permeability are among the parameters used to describe the mass transfer for a specific combination of polymer and permeant [13]. Permeability is an important parameter for measuring the overall transfer rate through a polymer layer. The permeability coefficient can be expressed using a solubility coefficient (S) and a diffusion coefficient (D) as follows [27]:

$$P=SD=\frac{ql}{At\Delta p} \quad (1)$$

In Equation (1), S is a thermodynamic term describing the amount of permeant that can dissolve in the polymer. D is a kinetic term indicating the velocity of the permeant in a specific polymer host. In addition, it affects the time required to

reach steady state after diffusion. D is typically described by Arrhenius type equation as follows [27]:

$$D = D_0 \exp(-E_d / kT) \quad (2)$$

The size of the permeant influences the diffusion coefficient. Geometrical and thermal properties also affect the value of D . The size of the permeant and the porosity of the polymeric material will affect D_0 whereas the temperature will affect the exp term. The temperature change can also affect D_0 if temperature changes the porosity of the polymeric material. If D is low, either the permeants are relatively large, the polymer is tightly packed, or the temperature is low [13]. Parameter q is the quantity of permeant transferred by a unit of area (A) in a specific time (t). Parameter l is the thickness of the material, and Δp is the partial pressure difference. Permeability properties are additionally influenced by chemical structure, wettability, degree of free volume in the polymer, crystallinity, orientation, tacticity and crosslinking [30].

Fick's laws of diffusion quantitatively describe the permeation processes [27]. These laws describe the processes by which matter is transported from one part of a polymer film to another as a result of random molecular motions. Fick's first law, i.e. Equation (3) expresses the approximation of the transfer rate (F) of the diffusing substance per unit area in the steady state by D , the concentrations of the permeant molecules at opposite sides at the packaging wall (c_1 and c_2), and the direction of diffusion (x) as follows:

$$F = -D \frac{\partial c}{\partial x} \Rightarrow F = -D \frac{c_1 - c_2}{x} \quad (3)$$

Permeants in polymers often induce interactions. Swelling, plasticizing and even morphological changes can take place. When a large amount of permeant molecules enters the polymer matrix, it swells [31,32]. The swelling of the polymer by the permeant increases the diffusivity. With interacting penetrants the diffusion coefficient can vary as a function of the concentration and time due to swelling and plasticization of polymer [33,34]. This has usually a stronger effect on diffusion than on solubility.

3.2 Oxygen and water vapour barrier measurement

Term ‘barrier property’ refers to a material’s ability to resist the diffusion of specific species (molecules, atoms or ions) into and through itself. The barrier properties of polymeric materials are influenced by a wide range of variables, making conclusions regarding these properties sometimes difficult to draw [33,35]. With polymer films, permeability is affected by the chemical and physical structure of the polymer, the chemical structure and concentration of the permeant, temperature and humidity. In addition, the mechanical strength and barrier properties of amorphous or semicrystalline materials, such as polymers, are affected by their glass transition temperature (T_g) [12]. When the polymer is cooled below its T_g , it becomes hard and brittle. Above T_g the polymer is soft and flexible due to higher mobility of amorphous polymer chains. Many properties of both the polymer and the permeant affect gas and vapour permeation, and these must be taken into consideration when interpreting barrier results. The main factors are presented in Table 1 [36].

Table 1. The main properties of polymers and permeants affecting permeation.

Factor	Effect
Permeant size and shape	Small permeants permeate rapidly
Polarity	Impairs water vapour barrier properties
Polymer crystallinity	Less permeable due to fewer intermolecular spaces
Polymer orientation	The more ‘regular’ the polymer, the less permeable

There are many methods that can be employed for measuring gas and vapour permeability through polymers and polymer-coated boards [27]. Here, the objective was to determine oxygen and water vapour permeation properties measured as transmission rates through the samples.

The prevention of oxygen gas permeation is important because oxygen often permanently damages the quality of the packed item. Oxygen can be strongly and irreversibly absorbed into the polymers present in a food product [37]. The definition of oxygen transmission rate (OTR) is the quantity of O_2 gas passing through an area in a certain time under specified conditions of temperature, humidity and pressure [38]. In this work, the OTR values were measured mainly using Mocon Oxtran 2/20 equipment (Figure 2).



Figure 2. Equipment employed in measuring oxygen transmission rates.

In addition, a Systech M8001 unit was used for comparison of the obtained results. Polymer films and polymer-coated papers and boards were clamped into the diffusion cell, which was purged from residual O_2 using an oxygen-free carrier gas (N_2 added with 2% H_2). The carrier gas was routed to the sensor until a stable zero level was established. Pure O_2 was then introduced into the outside chamber of the diffusion cell. The flux of O_2 diffusing through the sample to the inside chamber was conveyed to the sensor by the carrier gas. The OTR was measured from two to eight parallel samples. The measurements were done using humid gases at room temperature (23 °C, 50% relative humidity) and the results were expressed as $cm^3/m^2/10^5 Pa/day$.

The water vapour transmission rate (WVTR) refers to the amount of water vapour transmitted through an area in a certain time under specified conditions of temperature and humidity. There are many standard procedures for measuring WVTR using gravimetric methods [39–43]. Here, the WVTR was measured using the gravimetric cup method, where the substrate is sealed in an absorbent ($CaCl_2$) containing cell and exposed to humid air in a controlled environment (Figure 3). This is the method most commonly used for determining the WVTR of polymeric materials [44].

3. Permeation through polymeric materials

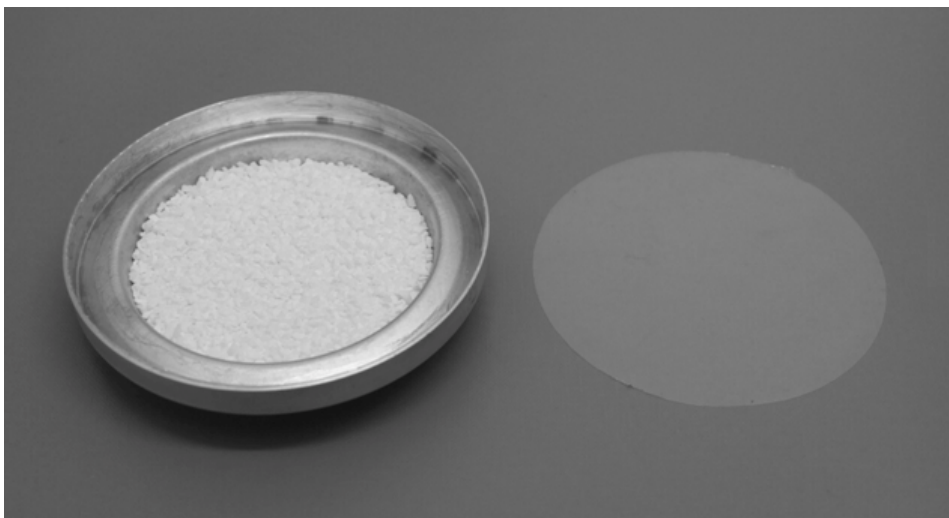


Figure 3. Aluminium dish employed in the determination of WVTR values.

The permeated compounds were collected on the low-concentration side of the cell, and the weight gain was monitored as a function of time. The WVTR values were measured from three to five parallel samples according to the modified gravimetric methods ISO 2528:1995 and SCAN P 22:68 and were expressed as $\text{g/m}^2/\text{day}$. The $\text{g/m}^2/\text{day}$ unit is not a standard SI-unit, but its use is justified on the basis that it is widely used in the industry to express WVTR values. The test conditions were 23 °C and 75% relative humidity. The WVTR of polymeric materials decreases exponentially with increased coating layer or film thickness if cracking of the barrier layer does not occur. Permeation takes place mainly through coating defects such as cracks, voids and pinholes or through the amorphous regions of polymer films [45]. In addition to layer thickness, the WVTR is affected by temperature and humidity, with the WVTR increasing with increased temperature and humidity [13]. The permeation process is also affected by the surface chemistry. Less polar surfaces are considered to improve water vapour barrier properties, as adsorption of polar water molecules is more difficult.

3.3 Reliability of OTR and WVTR measurements

The reliability of the obtained OTR and WVTR values may be hindered by a number of general sources of error, as described below. To minimize the impact of these errors, two to eight parallel samples were always fabricated and characterized. The number of parallel samples characterized depended on the variation of the obtained OTR and WVTR values between parallel samples. For this reason, the standard deviation value was also determined together with the average OTR and WVTR values obtained for an individual sample. When a low standard deviation value was obtained, the properties of the parallel samples were considered to be homogenous and the number of parallel measurements was smaller.

The main sources of error in OTR and WVTR measurements are due to the properties of the substrates. Permeability properties are greatly affected by the thickness and the coat weight of the sample [33,35]. In addition, the properties of the polymer itself and the coating method used influence the repeatability of the results. The coat weight and thickness of different polymeric substrates can vary greatly even within the same polymer sheet. The impact is usually greater when the substrates have been fabricated, for example, by a lab sheet coater or by solution casting. Commercial polymeric products are considered to be more homogenous, diminishing the variation of barrier properties between parallel samples. Sample heterogeneity increases mechanical stress in the polymeric material, possibly leading to increased numbers of defects. This may cause internal cracking of the sample material during measurement. In addition, to gain good repeatability of results, i.e. low standard deviation, carefulness in handling the samples is crucial due to the sensitivity of both the polymeric material and the thin Al_2O_3 coating. It was noted, that board-based samples were easier to handle due to the stiff base material.

The measurement conditions also affect the repeatability of the results, making stable conditions a necessity. However, some variation in temperature ($23\text{ }^\circ\text{C} \pm 0.1\text{ }^\circ\text{C}$) and humidity (relative humidity % $\pm 2\text{--}5\%$) may nevertheless occur, causing the polymer to shrink or swell. In WVTR measurement by the cup method the sample is sealed against the aluminium dish with hot wax. This can induce thermal stresses in some polymers. In addition, air escaping from the dish may cause bubbles in the wax layer, and impurities or hot wax may lead to poor adhesion between the wax seal and the aluminium dish. Such samples are to be rejected. In addition, as the WVTR measurement is based on change in

3. Permeation through polymeric materials

weight, there is a risk of error during weighing. Depending on the precision of the weighing appliance, a very low WVTR may require prolonging the weighing intervals. On the other hand, an extremely high WVTR can cause saturation of the salt within the dish, thus limiting the measurable values. In OTR measurement, however, side leakage, often referred to as the 'by-pass stream' or 'zero', can be determined. When measuring the properties of relatively good barrier materials, the detection limits of the measurements ($0.01 \text{ cm}^3/\text{m}^2/10^5 \text{ Pa/day}$ for OTR, $\sim 1 \text{ g/m}^2/\text{day}$ for WVTR [36]) set some limitations. In addition, it is beneficial to measure, for example, polymer-coated board or paper with the polymer layer facing the carrier gas stream. Due to the porous structure of the fibrous material the reverse set-up could cause lateral leakage of oxygen from the surrounding atmosphere along the material to the inside chamber. In addition, the carrier gas flow can pick up permeant molecules from the porous structure. In order to avoid leakage, the sample is sealed against the test cell with vacuum grease. However, this grease can spread onto the sample and affect the polymer properties. Based on the fact that the sources of errors described here were taken into account during this work, the OTR and WVTR values obtained are considered reliable.

Instead of using the cup method, the WVTR values could be measured with similar equipment as the OTR values. With this kind of equipment, the detection limit for water vapour can be as low as $5 \cdot 10^{-4} \text{ g/m}^2/\text{day}$ thus enabling the study of high barrier materials. As the minimum detectable WVTR with the cup method is $\sim 1 \text{ g/m}^2/\text{day}$, even with a perfect barrier the result would not be better. This was the main limitation concerning the use of the cup method.

The main difference between the cup method and several automated systems is the means of detection. While cup method is a gravimetric method, the others are usually based on chemical detection of water molecules. In addition, the automated systems utilize gas flows on both sample surfaces. The advantage of continuous gas flow is a constant concentration gradient over the sample. In cup method the salt absorbs the moisture and becomes eventually saturated. On the other hand, a continuous carrier gas flow can affect the results in the case of porous materials. Measuring low WVTR values is easier with an automated system, while the cup method allows a wide test range and several parallel measurements with lower investment costs. This is the case especially when dealing with moderate test conditions. High test temperature and humidity can cause softening of the wax sealant and fast saturation of the salt.

4. Deposition of high-quality thin-film barriers

4.1 Conventional barrier coatings

The oxides SiO_x and AlO_x are commonly used barrier coating materials for polymers in packages. SiO_x , in particular, has been used to replace aluminium foil in applications such as fibre-based packages for dry food mixes, drinks, sauces and seasonings, polymer composite cans, and packages for snacks, coffee and pet foods. Coatings of AlO_x have been used in applications, such as laminated heat-sealable packages for snack foods.

Industrial thin SiO_x coatings for packages are mainly fabricated using vacuum deposition techniques, such as sputtering, evaporation or plasma enhanced chemical vapour deposition (PECVD) [19,46]. In addition, plasma deposition has been used to apply films roll-to-roll from liquid precursors at atmospheric pressure with reasonable high speed. One configuration is that the plasma nozzles are moving in x-direction as the sample moves in y-direction. The distance from the sample to the nozzle head can be kept constant. Liquid precursor is atomized into droplets and sprayed directly into the plasma and then onto the substrate. The atmospheric plasma deposition technique for fabrication of barrier coatings has not yet been employed for industrial use. In PECVD the chemical reactions of vapour precursors take usually place on a batch-type vacuum reactor. However, the PECVD can also be employed also as roll-to-roll process at atmospheric pressure [47].

The sputtering, evaporation and PECVD techniques have been used to fabricate coatings with thicknesses of 10–100 nm on polymers. Of these techniques, the PECVD deposition technique gives the best barrier properties [19]. The fabricated SiO_x coatings are transparent, water-resistant and, in terms of barrier properties, comparable to metallic aluminium coatings. The problem

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with SiO_x coating is its poor mechanical resistance, which can be solved by varnishing or laminating [21]. The barrier properties of thin-film-coated materials depend strongly on the properties of the polymer. Gas permeation through thin-film-coated polymer is also affected by defects in the inorganic layer [48–53].

Besides the techniques mentioned above, a number of other deposition techniques can be utilized to fabricate thin SiO_x , AlO_x or metallic aluminium coatings onto polymers for various applications [21,54–75]. Relevant techniques for the present work (magnetron sputtering (MS), electron beam evaporation (EBE), sol-gel (SG) deposition, and atomic layer deposition (ALD)) are well described in literature [69–75], and in the case of Al_2O_3 coatings, in Publication I. The sol-gel coating (SG) technique as a wet chemical method differs from other, vacuum-based techniques discussed here. The technology is simple and can be applied as several different variants. However, industrially, these layers are typically thick, morphologically different and cannot be considered as thin film technology.

4.2 Atomic layer deposition (ALD)

The ALD technique is considered to be an advanced version of the CVD technique. There are many drawbacks with conventional CVD when fabricating thin films on polymeric substrates. The operating temperature range for a typical CVD process is around 300–500 °C, which is too high for sensitive polymers as it exceeds their melting point. In addition, with CVD the use of precursor gases cannot be effectively controlled and thus the thickness of the film cannot be tightly controlled. Some drawbacks, such as high deposition temperature, can be somewhat overcome with plasma-enhanced CVD. However, the film quality is typically poorer when the CVD or PECVD process is applied compared to ALD. CVD and PECVD leave defects and pinholes in the inorganic film [48,49,53,76]. The advantages of the ALD technique are the possibility to employ relatively low deposition temperatures and yet still grow thin films in a highly controlled manner. With ALD, the thin film grows layer-by-layer based on self-limiting gas-solid reactions. This technique is well suited to producing high-performance gas diffusion barrier coatings on porous materials as it allows the preparation of dense and pinhole-free inorganic films that are uniform in thickness even deep inside pores, trenches and cavities of various dimensions [63,68,77,78]. The layer-by-layer film growth and the surface saturation through chemisorption

enables precise control of the film growth and thickness [79,80]. This is the main difference between ALD and CVD; in CVD chemisorption is also applied but without surface saturation, making the growth primarily controlled by the dosage of the precursor.

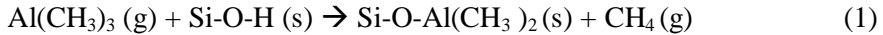
The chemical reactions take place in a vacuum chamber. The precursors are fed alternately into the chamber in vaporized form. The precursor pulses are separated by an inert gas purge. During the purge, unreacted excess precursor molecules are removed together with the gaseous by-products. After the purge, the surface is saturated with the first precursor and can react with the second one. Finally, the surface is purged again with inert gas and the ALD cycle is completed. The ALD technique was developed in the 1970s in Finland by Suntola and Antson [81]. The first applications for ALD were large-area flat panel electroluminescence displays. Nowadays a wide range of ALD-grown materials and applications have been developed, from catalysts to electroluminescent displays to microelectronics and beyond [82].

4.3 The ALD process for Al_2O_3 coatings

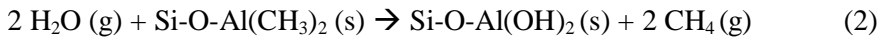
The focus of the present work was to grow Al_2O_3 films from trimethylaluminium (TMA; $\text{Al}(\text{CH}_3)_3$) and water (H_2O) or ozone (O_3). The TMA- H_2O process is considered to be a near-ideal ALD process and the reaction mechanisms are well understood. The chemical reactions involved in the formation of an Al_2O_3 layer on a silicon wafer substrate using H_2O and O_3 as an oxygen source are briefly discussed in the following [81,83–99]. Al_2O_3 is non-toxic and non-flammable and has a melting point of 2050 °C [90]. In controlled conditions Al_2O_3 forms highly even and uniform surface films, and is for this reason considered to be an excellent diffusion barrier. The growth of Al_2O_3 films is relatively straightforward by means of ALD. In this chapter, the fundamental reactions taking place during the TMA- H_2O process on smooth surfaces such as silicon wafer are briefly described.

Water vapour in the air is adsorbed onto most surfaces, forming hydroxyl (OH) groups. On silicon wafer, water vapour forms Si-O-H (s) groups. When the silicon wafer is placed in an ALD reactor chamber and TMA is pulsed into the chamber, the TMA (g) reacts with the Si-O-H (s) groups on the surface of the silicon as shown in reaction (1). Methane (CH_4 (g)) is simultaneously produced as a by-product.

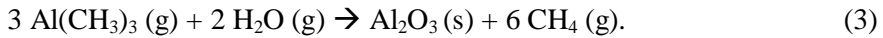
4. Deposition of high-quality thin-film barriers



The reaction continues until the surface is passivated with $\text{Si-O-Al}(\text{CH}_3)_2 (\text{s})$. TMA does not react with itself, which terminates the reaction to one layer. The deposition continues by pulsing H_2O into the reaction chamber. H_2O reacts with the methyl groups (CH_3) forming O-Al bridges and OH^- groups as shown in reaction (2). Again, CH_4 is produced as the by-product, and pumped away.

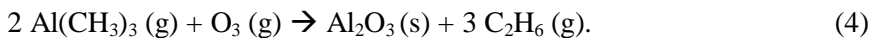


The excess H_2O again does not react with the OH^- groups, thus terminating the reaction to one atomic layer. After these two half reactions, one ALD cycle is completed. The whole ALD cycle can be described as reaction (3):



The number of surface OH^- -groups influences the number of chemisorbed species. Although considered near-ideal, there are some drawbacks to the TMA- H_2O process. Steric hindrance of precursors can influence on the film growth. In addition, the applied layer does not always form a fully smooth surface and the layer can have islets [80].

The use of O_3 instead of H_2O as the oxygen source is in some cases desired due to the higher activity of O_3 in ligand elimination [91]. Another reason for favouring O_3 is that it does not absorb as easily as H_2O into the reactor walls, thus facilitating purging. Due to these properties, better quality films could be obtained. On the other hand, a morphological characterization study [91] has shown that O_3 can also yield lower-quality films than H_2O . The films can be less dense and rougher, especially at low growth temperatures. When O_3 is used as the oxygen source for the preparation of Al_2O_3 films, the following reaction (4) is suggested to take place [92]:



The complex reaction mechanism and the use of O_3 in the fabrication of Al_2O_3 layers have been previously studied mainly for the needs of microelectronic applications [89,93–99]. It is assumed that during the O_3 pulse, O_3 decomposes into O_2 and monoatomic O which is the active species [91]. The efficiency of

this decomposition reaction is believed to be temperature-dependent [93]. The study of O_3 decomposition [91] showed that the use of O_3 could yield lower growth per cycle (GPC) rates compared to the corresponding H_2O process. The different growth mechanism and high reactivity of O_3 may result in a different film structure.

In a work by Goldstein *et al.* [98], the TMA- O_3 process at 90–377 °C was studied by in-situ measurements. It was revealed that CH_4 (g) and CO_2 (g) were the reaction by-products. In addition, it was recently noticed that besides CH_4 (g) and CO_2 (g), H_2O is also produced as a by-product in this process [99], and the researchers proposed a reaction mechanism where TMA chemisorbs on the surface, releasing CH_4 (g), and the following O_3 pulse partly combusts the remaining CH_3 (g) ligands to form CO_2 (g) and H_2O (g).

4.4 ALD fabricated barrier coatings

Applications for ALD-grown barrier coatings have previously been mostly related to electronics. In addition, the ALD-coated polymeric substrates have mainly been non-biodegradable. The most common ALD-grown gas and water vapour barrier material has been Al_2O_3 [63–65,68,77,100–102]. In these studies the Al_2O_3 films have mainly been fabricated using the TMA- H_2O process, but studies also show that O_3 can also be used as the oxygen source when depositing on polymers [103].

The advantages of ALD-grown Al_2O_3 coating are superior moisture protection and relatively low deposition temperature. For the purposes of protecting electronic parts, water vapour transmission rates of the order of 1×10^{-3} g/m²/day and oxygen transmission rates below 5×10^{-3} cm³/m²/10⁵ Pa/day were reported for less than 25 nm thick Al_2O_3 coatings on synthetic, non-biodegradable polymers [64]. In addition, Park *et al.* [77] reported a water vapour transmission rate of 0.03 g/m²/day at 38 °C and 100% relative humidity for an ALD-grown Al_2O_3 barrier that was 30 nm thick and deposited on both sides of a poly(ethersulfone) substrate, whereas Carcia *et al.* [68] showed that 25 nm thick Al_2O_3 barrier films on poly(ethylene naphthalene) substrates can have a water vapour transmission rate of less than 1×10^{-5} g/m²/day. These results are, however, only partly comparable with the results presented in the present study, in which the substrates are mainly biopolymeric materials.

The focus of this work is on the novel benefits of ALD-grown films as oxygen and water vapour barrier materials. Prior to this thesis, there have been no

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studies covering a wide range of different bio-based substrates combined with less than 100 nm thick ALD-grown Al_2O_3 layers. The barrier level required for food and pharmaceutical packaging applications is not as low as that needed for the protection of electronics. Barrier requirements for sensitive food products presented in Figure 4 have been reported to vary between 0.01 to 100 $\text{cm}^3/\text{m}^2/10^5$ Pa/day for OTR and 0.01 to 100 $\text{g}/\text{m}^2/\text{day}$ for WVTR [104].

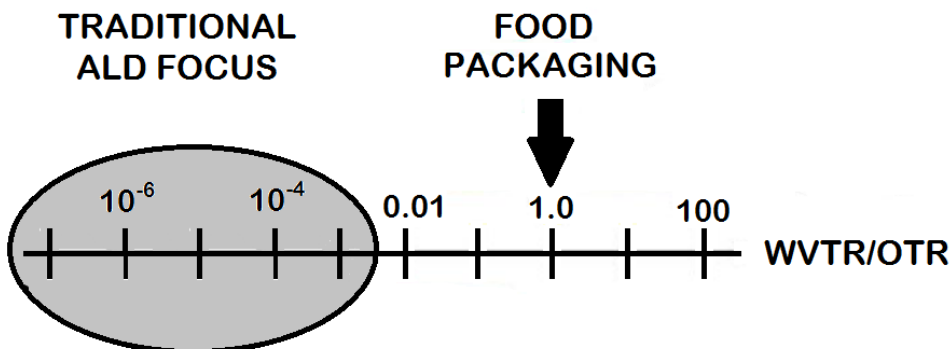


Figure 4. The oxygen and water vapour barrier level required for commercial applications (modified from Beneq Ltd marketing material).

The polymeric substrate materials employed in the present work are temperature-sensitive, which in practice makes thin layer formation more demanding, thus essentially limiting the number of possible ALD processes and ALD-grown coatings which can be applied on these materials as barrier layers. In addition, due to dust and other particles on the substrates, the ALD coatings on polymeric materials cannot be fabricated in a cleanroom environment. This also limits the use of impurity-sensitive ALD processes.

In this thesis the ALD-grown coating material was Al_2O_3 , although other ALD-grown oxides, such as silicon dioxide (SiO_2) [105] and titanium dioxide (TiO_2) [103], could also be employed as barrier layers. In addition, SiO_2 has been grown as a part of a nanolaminate structure. Nanolaminates are structures made up of alternating layers of different materials, and the properties of the nanolaminate usually differ from the properties of the individual materials used to build the nanolaminate structure. Nanolaminates using SiO_2 and Al_2O_3 have been found to improve barrier properties [65]. In addition, tungsten and Al_2O_3 nanolaminates have been grown for thermal barrier purposes [106].

Pure tungsten has also been deposited at 80 °C as gas diffusion barrier layers on polymer films and polymer particles [107]. Other metals, such as iridium, have been employed as copper diffusion barriers to prevent diffusion into silicon in copper interconnected structures [108]. ALD-grown nitrides, such as tungsten nitride (WN) [109], niobium nitride (NbN_x) [110], tantalum nitride (TaN_x) [111] and zirconium nitride (ZrN) [112] have been shown also to effectively prevent copper diffusion.

The most recent development in polymer related ALD research concerns molecular layer deposition (MLD). With MLD, organic-inorganic hybrid films can be grown by a sequential, self-limiting surface chemistry process by using an inorganic precursor, such as TMA, and an organic precursor, such as ethylene glycol [113]. These could have potential as barrier materials, especially in applications that demand flexibility.

5. Experimental

5.1 Objectives

The first task of this thesis was to study whether high-quality barrier coatings with similar or better barrier properties could be fabricated on polymeric materials by utilizing thin-film deposition methods other than ALD. The hypothesis was that of all thin-film deposition techniques, ALD provides the most defect-free films. Thereafter, the task was to perform the ALD coatings at 80, 100 or 130 °C on biopolymeric materials. This temperature range was selected based on the fact that most biopolymers are known to be temperature-sensitive. ALD-grown Al_2O_3 coatings were deposited onto several polymeric substrates at target thicknesses ranging from 10 to 900 nm. The ALD process parameters (most suitable oxygen source, deposition temperature, and film thickness) were optimized for these biopolymers. This enabled the investigation of the oxygen and water vapour barrier properties of the Al_2O_3 coatings on polymer films and polymer-coated papers and boards. An additional objective of the study was to improve the barrier properties of ALD-coated materials by employing treatments and coatings on the substrates prior to the ALD process.

5.2 Substrate materials

The objective was to study the influence of thin Al_2O_3 coatings on the barrier properties of polymeric materials, concentrating mainly on bio-based substrate materials. To focus on the impact of the coating, commercial polymeric materials were chosen as the main substrates. Commercial products have more homogenous surface chemistry, thus minimising the variation in properties between parallel samples. Commercial paperboards (provided by Stora Enso Oyj) with bio-based polylactide (B(PLA)) coatings on one side were used as the

main substrate materials. A wide range of other commercial polymer films were also used as substrate materials. In addition, non-commercial biopolymer materials were also used as substrate materials in order to widen the scope of investigation of potential ALD-coated materials. The materials employed are presented in Table 2. It should be noted that the barrier properties of the pristine substrate materials could not be compared as such due to differences in polymer layer thickness, coat weight, coating and film fabrication processes, possible additives such as plasticizers in the substrate materials, the base material type, e.g. paper and board, and surface roughness values.

Table 2. Packaging materials employed in the present work as substrates.

Code	Description	Commercial	Publication
B1(PLA)	Polylactide-coated board; PLA 35 g/m ² on board 310 g/m ²	x	I, III, IV
B2(PLA)	Polylactide-coated board; PLA 35 g/m ² on board 210 g/m ²	x	II, III
B3(PLA)	Polylactide-coated board; PLA 27 g/m ² on board 210 g/m ²	x	III, V
B(GGM)	Galactoglucomannan-coated board; GGM approx. 9 g/m ² on pigment-coated board 200 g/m ²		III
B(PE)	Low-density polyethylene-coated board; LDPE 15 g/m ² on board 210 g/m ²	x	I–V
P(UNC)	Uncoated paper; 80 g/m ²	x	II
P(PIG)	Pigment-coated and calendered paper; 60 g/m ²	x	II
P(LDPE)	Low-density polyethylene-coated paper	x	II
PLA1	Polylactide film; 20 µm	x	III, VI
PLA2	Polylactide film; 75 µm	x	III
PLA3	Polylactide film; 25 µm	x	II
NFC	Nanofibrillated cellulose film; approx. 60 g/m ²		III
PHB	Polyhydroxybutyrate film; 180 µm	x	III
Pectin	Pectin film; 160 µm (solution-casted)		III
PEN	Polyethylene naphthalene film; 50 µm	x	II
PP	Polypropylene film; 30 µm	x	II
PET	Polyethylene terephthalate film; 50 µm	x	II

5.3 Thin-film depositions

Besides ALD, other thin-film deposition techniques were employed in the present work, including magnetron sputtering (MS), electron beam evaporation (EBE) and sol-gel (SG) coating. These techniques were chosen for the comparison of the ALD technique as they are widely studied and also used in commercial barrier applications. In addition, the chosen deposition methods are thought to be more cost-efficient and faster than conventional batch-type ALD. The techniques also enabled the fabrication of thin Al_2O_3 coatings at relatively low temperature. The depositions were made at 100 °C on B1(PLA). The deposition processes are described in detail in Publication I.

The ALD coatings were mainly done with a SUNALE R-200 reactor from Picosun presented in Figure 5. The target thicknesses of the fabricated Al_2O_3 coatings (25–100 nm) were as similar as possible for all of the thin-film deposition techniques used.



Figure 5. During this thesis VTT invested in a new SUNALE R-200 ALD-reactor which is not limited by clean room conditions.

Due to differences in the controllability of the processes, some variation between sample thicknesses did nevertheless occur. The best control of Al_2O_3 coating thickness was achieved with the vacuum-based methods (MS, EBE and ALD). In contrast, precise thicknesses were difficult to achieve using SG coating due to the nature of the coating application method (spraying). For example, with 100 nm Al_2O_3 coatings, the thickness varied 10–15% from the target thickness. Of the studied methods, ALD enabled the most precise control of film thickness. The levels of control and film quality enabled by ALD are unobtainable with the other studied thin-film deposition techniques. Furthermore, it should be noted that purely inorganic Al_2O_3 coatings are not possible to fabricate using the SG technique due to the presence of organic molecules from the precursor solution in the deposited film. In addition to Al_2O_3 coatings, pure aluminium films were also grown using the MS technique. This was included in the study because metallic Al, as a thicker film, is considered to be a high performance barrier.

5.4 Pre-treatments for polymeric materials

Pre-treatments (corona and thermal) were employed to improve the surface properties of the polymeric materials prior to the ALD process. Corona treatment is an electrical process utilizing ionized air to increase the polarity of the surfaces by oxidation. The surface is bombarded with O_3 , O_2 and free O radicals in order to increase the surface energy and lead, potentially, to higher quality coatings. In this work, the hypothesis was that the increased polarity could increase adhesion between the polymer surface and the first ALD-grown Al_2O_3 layer, possibly enabling the growth of a more uniform Al_2O_3 coating. The corona treatment was performed on B(PE) and B1(PLA) substrates using a widely used method [114]. After the corona treatment, the substrate materials were coated with Al_2O_3 at 100 °C.

The barrier properties of polymeric films or coatings are affected by their chemical structure and morphology [115]. The impact of thermal treatments on barrier properties has been previously studied [116,117]. With extruded PLA-coatings, polymer crystallinity has been found to be inversely related to the difference between the melt temperature and the quenching temperature [118] leading sometimes to formation of a totally amorphous structure. Diffusion of gas permeants occurs through the amorphous regions, while crystalline regions are more or less impermeable. The WVTR of PLA decreases with increasing crystallinity [119]. Drawing on these findings, the idea of the current work was

5. Experimental

to utilize the ability of thermal pre-treatment to increase crystallinity and thus to improve the barrier properties of the substrate prior the Al_2O_3 coating and possibly to even out the surface chemistry and topography due to more ordered polymer structure. The B3(PLA) substrate was thermally treated in a convection oven at 130 °C for 4, 9 or 16 minutes followed by quenching at room temperature. After thermal treatment, the substrate materials were coated with a 25-nm-thick Al_2O_3 layer grown by ALD at 80 °C.

5.5 Pre-coatings prior to ALD- Al_2O_3 coating

Besides pre-treatments, the barrier properties of polymeric materials can be improved by pre-blocking the largest pinholes in the substrate using a coarser method than ALD. In addition, pre-coatings can be utilized to alter the surface topography prior to ALD. In this study, the pre-barrier layers were generated using two separate methods; layer-by-layer (LbL) deposition of polyelectrolytes [120,121], and sol-gel deposition of an epoxy-coating (epoxy-SG). The epoxy-SG coatings with a target coat weight of 2 g/m² were prepared using 3-(trimethoxysilyl)propyl glycidyl as the epoxy source, ethanol as a solvent, and water as an initiator for the hydrolysis and condensation reactions. The coatings were applied on corona pre-treated B2(PLA) surfaces using a spraying method, dried at 120 °C and further coated with an ALD-grown Al_2O_3 layer at 80 °C. A corona treatment unit (ET1 from Vetaphone) with a treatment time of 60 seconds was used for better wetting and adhesion properties between the coating and the substrate.

The polyelectrolyte multilayer (PEM) films from sodium alginate (ALG) and chitosan (CHI) were fabricated according to the LbL method on PLA1. The samples were coated with an ALD-grown Al_2O_3 layer at 100 °C.

5.6 Sample characterizations

Thermogravimetric (TG) analyses were employed to reveal the possible thermal limitations of different polymer coatings for use as substrates for thin-film depositions. Scanning electron microscopy (SEM) and atomic force microscopy (AFM) were used to image surfaces and their roughness. In addition, AFM acquires information on surface topography, friction, and adhesion [122]. For Publication II, the SEM employed was a Hitachi S-3400 N VP-SEM with an operating voltage of 15 keV, and for publications III and VI a JEOL JSM-

7500FA was used. In Publication II, a multimode scanning probe AFM (Nanoscope III from Digital Instruments Inc.,) was employed, and in publications I, III and V an AFM XE-100 (Park Systems with 905-ACTA cantilever) was used. Non-contact ‘tapping’ mode was used for the AFM imaging [123,124].

The thin-film film growth rates and actual film thicknesses on the polymeric substrates could not be directly measured. Instead, the film thicknesses and the ALD layer growth rates were estimated with a Nanospec AFT4150 reflectometer, ellipsometer or UV-Vis spectrophotometer from films grown on a silicon Si(100) wafer. The surface coverage of ALD-grown Al_2O_3 layers were determined by X-ray photoelectron spectroscopy (XPS) analyses. The amount of Al in the Al_2O_3 layers was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis.

The effects related to pre-treatments and pre-coatings were characterized by contact angle (CA) and surface energy measurements. The CA measurement is the oldest and still the most popular method of evaluating wettability [125]. Wide-angle x-ray scattering (WAXS) was utilized to study the level of crystallinity of the substrates due to its allowance of the characterization of distinctions between different polymers [126]. The molecular weights of the components in the PEM film were determined by viscosity and density measurements. The Mark–Houwink equation (4) gives a relation between intrinsic viscosity $[\eta]_{in}$ and molecular weight M_v by utilizing the Mark–Houwink parameters K and a [127–131].

$$[\eta]_{in} = KM_v^a \quad (4)$$

Although many characterization methods were employed during the research, the emphasis was on oxygen (OTR) and water vapour transmission (WVTR) rates. Table 3 presents the main characterization methods employed and the information obtained.

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Table 3. Characterization methods applied and the information obtained.

Method	Information obtained	Publication
Thermogravimetric analysis (TG)	Polymer degradation temperature	II
Scanning electron microscopy (SEM)	Structure and thickness of the Al ₂ O ₃ coating	II, III, VI
Atomic force microscopy (AFM)	Structure, morphology and roughness of the polymeric material prior to and after Al ₂ O ₃ coating	I–III, V
Scanning ellipsometry	Al ₂ O ₃ coating thickness (20–100 nm)	I, II, VI
UV/Vis spectrophotometer	Al ₂ O ₃ coating thickness (50–100 nm)	I, III, V
Reflectometer	Al ₂ O ₃ coating thickness (25–100 nm)	I, III–VI
X-ray photoelectron spectroscopy (XPS)	Polymer surface coverage by the Al ₂ O ₃ coating	II
Inductively coupled plasma atomic emission spectroscopy (ICP-AES)	Amount of Al in the Al ₂ O ₃ coating	I
Contact angle (CA)	Surface wetting	III–VI
Surface energy (γ_s)	Surface polarity	III–V
Wide-angle x-ray scattering (WAXS)	Surface morphology	V
Microviscometer and density meter	Molecular weight of the polyelectrolyte	VI
Oxygen transmission rate (OTR)	Oxygen barrier property of the sample	I–V
Water vapour transmission rate (WVTR)	Water vapour barrier property of the sample	I–VI

6. Results and discussion

6.1 Characterization of thin Al₂O₃ coatings grown on polymers

6.1.1 Properties of polymeric substrates

The main scope of the present work was to investigate whether ALD-grown Al₂O₃ coatings could extend the use of polymeric materials as oxygen and water vapour barriers. The substrate materials were mainly bio-based, although some synthetic, non-biodegradable polymeric materials were also investigated. It should be noted, that the pristine substrates could not be compared as such. The surfaces of different polymeric materials vary greatly, due mainly to different coating methods and coat weights and the effect of these on material thickness and surface smoothness. Figure 6 shows AFM images of the surfaces of the two most studied substrate materials in publications related to this thesis, B(PE) and B1(PLA).

6. Results and discussion

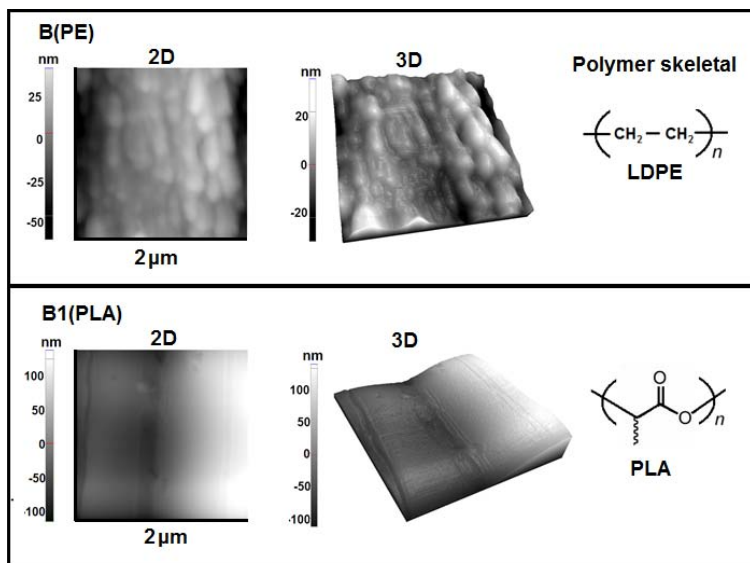


Figure 6. AFM images (2D and 3D) of LDPE-coated and PLA-coated board.

Thermogravimetric (TG) analysis was employed to investigate the degradation temperature of the different polymers and polymer-coated papers and boards. This was done in order to investigate whether these materials could be used as substrates in thin-film depositions. The TG analysis employed on the majority of the polymeric materials confirmed that the materials tested did not degrade thermally at the temperatures used in the low-temperature ALD experiments, i.e. below approximately 150 °C.

The resultant TG curves in air and in nitrogen atmospheres are presented in Figure 7. The polymeric materials behaved quite similarly. Degradation occurred at a slightly higher temperature in nitrogen atmosphere compared to air. The first endothermic step, water removal, began at room temperature and continued at higher temperatures. The materials decomposed in a single step at temperatures ranging from 300 to 450 °C. Decomposition in nitrogen was not completed for PEN and PET at 450 °C. The final step, carbon combustion, was highly exothermic. This was naturally observed only in air, i.e. in the presence of oxygen.

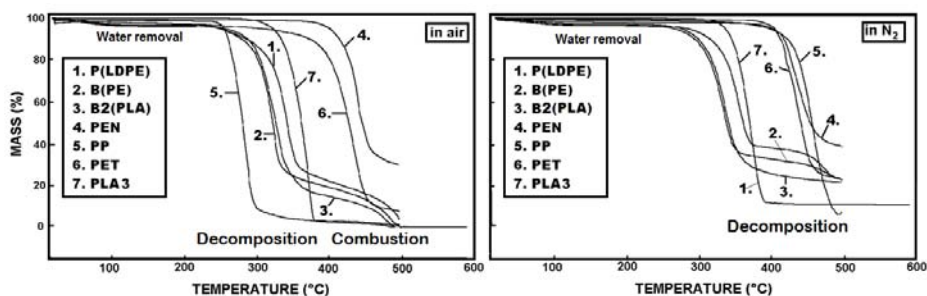


Figure 7. TG curves recorded for polymeric materials in air and nitrogen atmospheres.

6.1.2 Comparison of barrier properties obtained by different thin-film deposition techniques

It is evident based on earlier studies [63–65,68,77,100–102] that ALD-grown Al_2O_3 coating significantly improves the oxygen and water vapour barrier properties of various conventional i.e. petroleum-based polymer films. In this study, however, the scope was on bio-based substrates. It was observed that although the barrier properties were improved with Al_2O_3 coatings fabricated by all of the compared thin-film deposition techniques, with the thinnest coatings (25 nm), the improvement was the largest with the ALD technique (Table 4). This is mainly due to the nature of the ALD process. The other thin-film deposition techniques leave defects and pinholes in the Al_2O_3 coating but the ALD technique produces pinhole-free coatings even on porous materials in a highly controlled manner.

Table 4. Comparison of deposition techniques for the production of efficient barrier coatings.

OTR ($\text{cm}^3/\text{m}^2/10^5 \text{ Pa/day}$)				
Sample	ALD	MS	EBE	SG
B1(PLA) uncoated	420 ± 10	420 ± 10	420 ± 10	420 ± 10
B1(PLA) + 25 nm Al_2O_3	20 ± 3	75, 245*	150 ± 10	460 ± 10
B1(PLA) + 50 nm Al_2O_3	60 ± 5	25, 145*	300 ± 140	400 ± 10
B1(PLA) + 100 nm Al_2O_3	200 ± 40	65 ± 1	210 ± 15	370 ± 10
B1(PLA) + 50 nm Al	-	26 ± 1	-	-
WVTR ($\text{g}/\text{m}^2/\text{day}$)				
B1(PLA) uncoated	64.9 ± 1.6	64.9 ± 1.6	64.9 ± 1.6	64.9 ± 1.6
B1(PLA) + 25 nm Al_2O_3	1.4 ± 0.2	11.0 ± 0.5	25.9 ± 2.7	62.5 ± 1.0
B1(PLA) + 50 nm Al_2O_3	1.8 ± 0.5	0.5 ± 0.1	21.8 ± 4.2	62.3 ± 1.9
B1(PLA) + 100 nm Al_2O_3	29.1 ± 5.1	1.9 ± 0.6	21.6 ± 7.1	62.0 ± 0.6
B1(PLA) + 50 nm Al	-	1.3 ± 0.5	-	-

*For samples coated with 25 nm or 50 nm thick MS- Al_2O_3 layers the standard deviation for OTR could not be calculated due to high variation in the values obtained.

Based on the results, a thin Al_2O_3 coating had a positive effect on both the OTR and WVTR values. Most impressively, when coating B1(PLA) with a 25-nm-thick Al_2O_3 layer by means of ALD, both the OTR ($20 \text{ cm}^3/\text{m}^2/10^5 \text{ Pa/day}$) and WVTR ($1.4 \text{ g}/\text{m}^2/\text{day}$) values were excellent. In terms of oxygen barrier properties, this sample performed better than an equivalent sample coated with 50 nm thick metallic aluminium using the MS technique ($26 \text{ cm}^3/\text{m}^2/10^5 \text{ Pa/day}$). The results imply that a 50-nm or thicker ALD-grown layer cracks more readily than a 25-nm-thick layer. These results justify the use of 50 nm or thinner ALD-grown Al_2O_3 coatings in further studies.

6.2 ALD growth process for Al_2O_3 coatings on polymeric materials

A second task related to thin-film deposition was to optimize the Al_2O_3 process by means of ALD for a range of non-biodegradable and bio-based temperature-sensitive substrates. The main focus was nevertheless on bio-based substrates. In the preliminary experiments, the ALD process parameters, i.e. deposition temperature (80, 100 or 130 °C) and choice of oxygen source (H_2O or O_3), were

investigated. Interestingly, the growth per cycle (GPC) values for the H₂O and O₃ processes were found to be nearly identical, i.e. 0.1 nm/cycle (as measured for films grown on silicon substrates). This disagrees somewhat with the findings of Elliot *et al.* [91], who report lower GPC values for the TMA-O₃ process compared to the TMA-H₂O process. It seems that here the O₃ gas might have been wet; note that the H₂O present may act as a catalyst for the reactions during the TMA-O₃ process, increasing the GPC value. According to Elliot *et al.* [91], the combination of both O₃ and H₂O could increase GPC closer to the GPC value of films fabricated using H₂O alone as the oxygen source. It should be emphasized that due to the different surface chemistries of different polymers, the actual growth rates may deviate from that determined for Al₂O₃ coating on silicon wafer [63,132].

The results obtained by ellipsometry indicate that for relatively smooth polymer films with low anisotropy, the thickness of the ALD-grown Al₂O₃ coating is close to the thickness determined on silicon wafer. However, other studies have shown that when coating polymers with ALD-grown Al₂O₃ layers, a nucleation period occurs within the first layers due to an insufficient amount of surface groups to initiate growth [133]. For example, polyethylene is a saturated hydrocarbon that lacks the typical chemical functional groups, such as hydroxyl species, that are necessary to initiate the growth of an inorganic film.

The growth of Al₂O₃ coatings on polymeric substrates was investigated by ICP-AES, XPS and SEM. The ICP-AES analyses were carried out to determine the amount of aluminium in the ALD-grown Al₂O₃ layers deposited on B(PE) and B1(PLA) using TMA and H₂O as precursors. Due to different surface roughness values, the substrates accommodate different amounts of Al₂O₃ during the ALD process. During Al₂O₃ depositions aimed at 25, 50 and 100 nm thickness, the B1(PLA) substrate was found to accommodate 96, 377 and 637 mg/m² and the B(PE) substrate 128, 836 and 858 mg/m² of aluminium, respectively. One explanation could be that when comparing to the smoother B1(PLA), B(PE) has a larger specific surface area and, accordingly, a larger number of surface sites to accommodate a larger number of molecules during ALD deposition (see Figure 6). The results are in agreement with the finding that the final thickness of the ALD-grown Al₂O₃ coating somewhat varies from the thickness determined with silicon wafer [63,132]. Another explanation could be the different nucleation periods in the beginning of the Al₂O₃ growth on different polymers due to the indiffusion of precursors into polymers [133].

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The XPS analyses performed on samples with 25 nm thick Al_2O_3 coatings fabricated using TMA and H_2O as precursors were based on surface distribution of elements [134–137], and they were employed to evaluate the surface coverage of the Al_2O_3 coating. The XPS data confirmed that the substrate had been covered quite effectively with a homogenous layer of Al_2O_3 within the XPS detection depth range (2–10 nm). Even highly porous surfaces such as pigment-coated paper P(PIG) were covered with a uniform layer of Al_2O_3 . The SEM images confirmed the data from the XPS analyses, showing that the deposited Al_2O_3 layers were homogeneous in thickness also in the substrate pores. This was also achieved with very thick Al_2O_3 layers on highly porous paper samples. Figure 8 shows a cross-sectional SEM image from uncoated paper P(UNC) with a 900-nm-thick Al_2O_3 coating. The figure also shows a top surface image from pigment coated paper P(PIG) with a Al_2O_3 coating aiming at 900 nm thickness. The thickness of this Al_2O_3 layer was found to vary from 980–1050 nm.

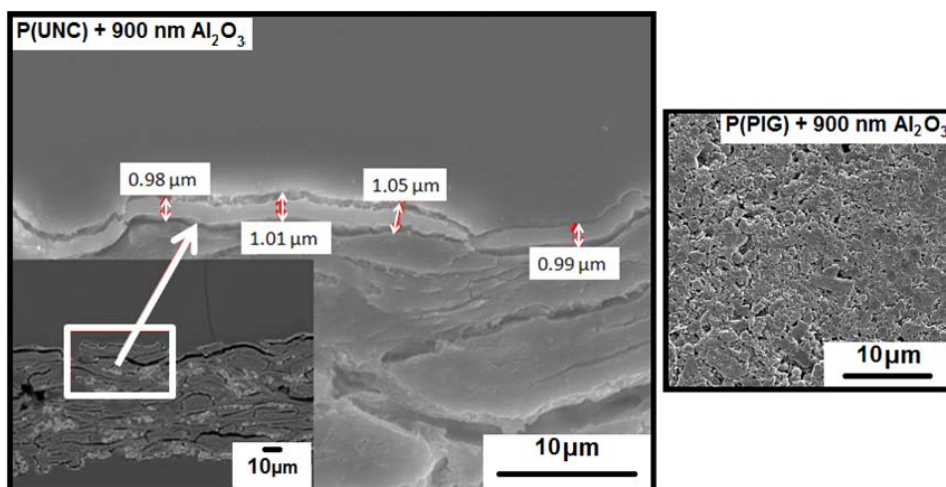


Figure 8. Images from P(UNC) and P(PIG) samples coated with 900 nm Al_2O_3 layers.

Surface coverage with Al_2O_3 was also demonstrated with nanofibrillated cellulose (NFC) fibres. The structure of NFC film resembles a fibre network. It was observed that a 25-nm-thick Al_2O_3 layer grown using the TMA- H_2O process could coat individual fibres. Figure 9 shows nanofibrillated fibres fully coated with Al_2O_3 . The cohesiveness of the Al_2O_3 coating was verified by determining the elements of the sample surface by energy dispersive spectroscopy (SEM-EDS). The smallest observed fibre thickness was approximately 50 nm with the curve radius from the fibre ends being approximately 25 nm. The ability to uniformly coat single fibres opens the potential for new applications in the area of filter development. Such materials are currently of great interest because of the combination of controlled integration of organic fibres and inorganic thin-film [138].

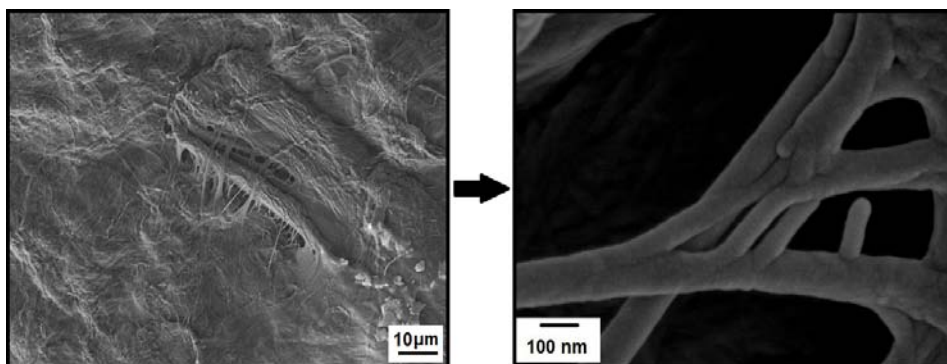


Figure 9. SEM image (*left*) with magnification (*right*) of Al_2O_3 -coated NFC fibre network possibly suitable for use in the area of filter development.

6.3 Barrier properties of ALD- Al_2O_3 coatings on biopolymeric materials

The task here was to study the improvement in the oxygen and water vapour barrier properties of mainly commercial biopolymeric materials brought about by ALD- Al_2O_3 coatings. In addition, non-commercial biopolymeric materials were used as substrate materials in order to widen the scope of investigation of potential ALD-coated materials. Because of the covalent bonding, the adhesion of metal precursor, such as TMA, to the substrate should be good even if the substrate lacks typical chemical functional groups such as hydroxyl ($-\text{OH}$) species [139,140]. Typically biopolymers have functional surface groups which

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can improve the adhesion between the substrate and the Al_2O_3 layer. This makes biopolymeric materials interesting substrates for ALD coatings.

In preliminary experiments conducted for process optimization purposes, two PLA-coated board samples, B1(PLA) and B2(PLA), were investigated. The deposition parameters considered were deposition temperature (80, 100 or 130 °C) and choice of oxygen source (H_2O or O_3). The results from the OTR and WVTR experiments with variously grown Al_2O_3 coatings are shown in Table 5. The deposited amount was 250 cycles aiming for a 25-nm-thick Al_2O_3 coating. To optimize the thickness, some B1(PLA) samples were also deposited with 100 cycles aiming for 10 nm. The variables investigated were temperature, oxygen source and film thickness. The results are given as average \pm standard deviation of two to three parallel measurements.

Table 5. Comparison of different process parameters' (temperature, number of deposited cycles and oxidant) influence on barrier properties.

Sample	OTR ($\text{cm}^3/\text{m}^2/10^5 \text{ Pa/day}$)	WVTR ($\text{g}/\text{m}^2/\text{day}$)
B1(PLA) uncoated	420 ± 10	65 ± 2
B1(PLA) + 25 nm Al_2O_3 by O_3 (100 °C)	12 ± 1	5 ± 2
B1(PLA) + 25 nm Al_2O_3 by H_2O (100 °C)	20 ± 3	1 ± 0.2
B1(PLA) + 25 nm Al_2O_3 by H_2O (130 °C)	107 ± 12	3 ± 2
B1(PLA) + 10 nm Al_2O_3 by H_2O (100 °C)	48 ± 5	11 ± 3
B2(PLA) uncoated	400 ± 9	75 ± 2
B2(PLA) + 25 nm Al_2O_3 by O_3 (100 °C)	2 ± 0.2	1 ± 0.2
B2(PLA) + 25 nm Al_2O_3 by O_3 (80 °C)	3 ± 1	7 ± 2
B2(PLA) + 25 nm Al_2O_3 by H_2O (80 °C)	6 ± 1	3 ± 1

Independent of the deposition parameters used, the 25-nm-thick ALD- Al_2O_3 coating remarkably improved both the oxygen and water vapour barrier properties of the PLA-coated board samples. For example, it was found with B1(PLA) that after 250 ALD cycles of TMA- O_3 carried out at 100 °C the OTR value improved from 420 to $12 \text{ cm}^3/\text{m}^2/10^5 \text{ Pa/day}$ and WVTR from 65 to $5 \text{ g}/\text{m}^2/\text{day}$. The improvement was from 420 to $20 \text{ cm}^3/\text{m}^2/10^5 \text{ Pa/day}$ and from 65 to $1 \text{ g}/\text{m}^2/\text{day}$ when using H_2O instead of O_3 . The 10 nm layer was found to be too thin to form a sufficient barrier layer on B1(PLA). One explanation could be that for Al_2O_3 coatings this thin, the indiffusion of precursors into polymers

during the nucleation period could affect more on the film growth than i.e. with 25 nm thick Al_2O_3 coatings [133].

With O_3 , somewhat better oxygen barrier properties may be achieved for bio-based substrates than in the case of the TMA- H_2O process. In the case of B2(PLA), similar improvements were noticed at 80 °C. The OTR value improved from 6 to 3 $\text{cm}^3/\text{m}^2/10^5\text{Pa}/\text{day}$ after 250 deposition cycles made using O_3 instead of H_2O .

The choice of deposition temperature (in the temperature range 80–100 °C) may not be crucially important. However, 130 °C was noticed to enhance the oxygen barrier properties significantly less than lower temperatures, indicating that 130 °C is too high a deposition temperature for these substrates. Although here, the deposition temperature (80–100 °C) was not the most effecting factor on the water vapour barrier properties, there are studies showing that the deposition temperature has a considerable impact on the topography, morphology as well as the adhesion to the Al_2O_3 coating of the polymeric substrates [141]. The increased crystallinity of the polymers caused by the higher temperature can cause brittleness for polymer structures which could then lead to cracking of the polymer layer impairing the barrier properties. The use of even lower deposition temperature than 80 °C could prevent the curling effect due to polymer shrinkage and could cause most improved barrier properties. In addition, the better adhesion between the polymer surface and the Al_2O_3 coating could be obtained by using lower deposition temperatures due to lower mobility of polymer chains during and after the deposition. In the study by Lahtinen *et al.* [141], polymers became brittle and the surfaces suffered considerable alterations in the process due to the process temperature on 100 °C influencing on the barrier performance. This led to easier routes for water vapour and oxygen to pass through the structures. The use of lower reactor temperatures could prevent cracking and enhance the barrier performance in terms of more controlled surface topography and polymer morphology.

It should be noted that the minimum detectable WVTR with the cup method is $\sim 1 \text{ g}/\text{m}^2/\text{day}$, meaning that even with a perfect barrier the result would probably be the same. Thus the barrier may be better than this but the standard deviation may also be higher.

Furthermore, both of the processes, TMA- H_2O and TMA- O_3 , seem to work well, at least for PLA-coated boards. As seen in Table 5, the OTR values achieved are somewhat better in the case of the TMA- O_3 process, whereas the opposite seems to be true for the WVTR values. During the water pulses,

absorbed H_2O may cause the polymer to swell, which should not be the case with O_3 . Hence, with the exception of the most sensitive materials which might not withstand the strong oxidation power of O_3 , the TMA- O_3 process can be considered a highly potential alternative for depositing Al_2O_3 coatings on biopolymers.

The moisture within the polymer chains of the substrate material should also be considered. This is especially the case with natural polymers, as these substrates tend to contain absorbed moisture. Removal of this moisture could enhance barrier properties because absorbed water can act as a plasticizer, thus deteriorating the material's barrier properties. The possible benefit of substrate moisture removal prior to ALD- Al_2O_3 deposition was investigated by keeping a B1(PLA) sample in a heated ($100\text{ }^\circ\text{C}$) ALD reactor chamber overnight before coating it with Al_2O_3 at $100\text{ }^\circ\text{C}$ using the TMA- H_2O process. The overnight thermal treatment resulted in a slight improvement in the OTR value: the value decreased from 20 to $8\text{ cm}^3/\text{m}^2/10^5\text{ Pa/day}$. However, the effect on the WVTR value was the opposite: it increased from 1 to $7\text{ g}/\text{m}^2/\text{day}$. This could be due to the different interactions that water vapour and oxygen induce in polymers [33,34]. Thus polymer swelling, plasticizing and possible morphological changes – in addition to film defects – could have different influences on the OTR than on the WVTR.

The removal of the moisture within the polymer chains reduced the plasticization effect of the water in the polymer, making the sample brittle.

The oxygen and water vapour barrier results achieved for a variety of biopolymer substrates with a 25-nm-thick Al_2O_3 layer deposited by the TMA- H_2O process are summarized in Figure 10. Note that H_2O was used as the oxygen source instead of O_3 to ensure that the results would not be distorted by the possible harmful effects of O_3 in the case of the most sensitive biopolymer film substrates. The depositions were made at 80 or $100\text{ }^\circ\text{C}$ depending on the expected temperature tolerance of the substrate material. From Figure 10, it can be concluded that ALD- Al_2O_3 -coated PLA2, pectin, NFC, B1(PLA) and B(GGM) samples are highly promising oxygen barriers with OTR values already at the commercial oxygen barrier level for dry food applications. Besides being a good oxygen barrier, the Al_2O_3 -coated B1(PLA) sample is also a highly promising water vapour barrier.

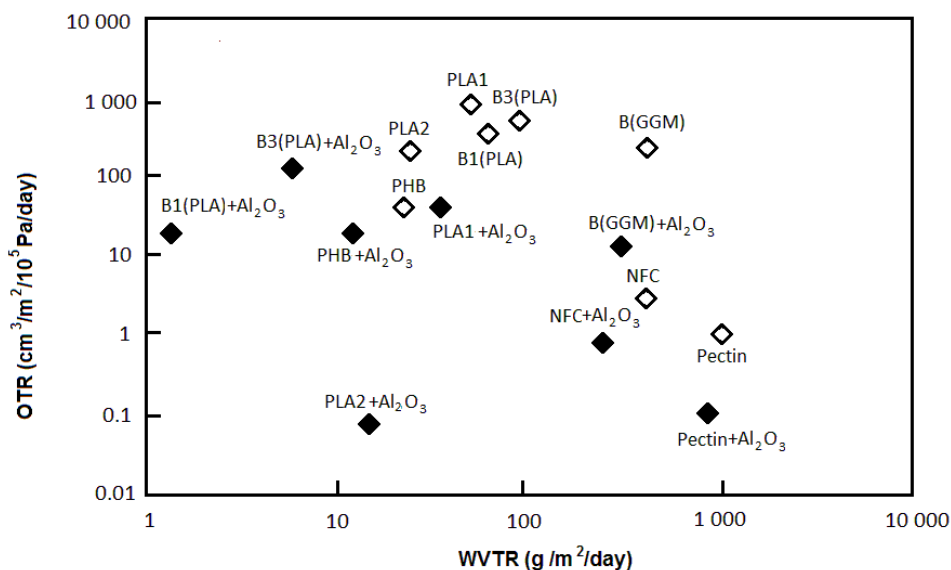


Figure 10. Best barrier results of bio-based materials achieved by coating substrates with a 25-nm-thick Al₂O₃ layer using the ALD process.

In addition to results presented in the Figure 10, similar Al₂O₃ coatings have been employed to a fibre-based substrate that has been coated with 15 g/m² petroleum-based low-density polyethylene. It was noticed that for this substrate a thicker Al₂O₃ coating was needed to improve properties considerably. The results from the barrier measurements showed that a 50-nm-thick Al₂O₃ coating decreased the OTR value from 7900 to 2700 cm³/m²/10⁵ Pa/day. The WVTR value was decreased from 7.0 to 2.0 g/m²/day.

With the cup method, the WVTR measurement of pristine petroleum-based polymer films, such as LDPE, PEN or PET is difficult because these materials are already good water vapour barriers even without the Al₂O₃ coating. The improvement in WVTR by the Al₂O₃ coating remains often unrecognized due to the high detection limit. However, the OTR values of petroleum-based polymer films, such as 30 µm thick PP and 50 µm thick PET films, have been measured. The results showed that a 25-nm-thick Al₂O₃ coating decreased the OTR value of PP from 1250 to 170 cm³/m²/10⁵ Pa/day and PET from 24 to 11 cm³/m²/10⁵ Pa/day (Publication II).

With some polymeric substrates a temperature of even 80 °C may be too high to produce the best barrier properties [141,142]. This may also be the case with

some biopolymeric substrates and, as a result, the development of ALD processes at temperatures closer to 50 °C is essential.

Although the scope of the research here was oxygen and water vapour barrier properties, the results open up the potential for new applications in addition to dry food and pharmaceuticals. Similar coatings on non-biodegradable polymers have been shown to also reduce the permeability of other gases, such as CO₂ [142].

6.4 Influence of pre-treatments and pre-coating layers on barrier properties

6.4.1 Enhanced surface polarity by corona treatment

Corona pre-treatment was employed to improve the surface properties of the polymeric materials prior to the ALD process. The possible effect of increased surface polarity on barrier properties was studied. The effect of corona treatment on surface polarity is considered to alter during time [143]. In the case of polymer films or coatings for packages, the treatment is therefore usually employed at the production line. The treatment was consequently investigated over a seven-day period to determine its potential long-lasting impact. The effect of pre-treatments was greater on B(PE) than on B1(PLA). With the corona treatment, the contact angle value of B(PE) decreased from 90 to 67° and remained at this level for seven days.

The increased hydrophilicity also improved the oxygen and water vapour barrier properties after the ALD-grown Al₂O₃ layer. The effect could be a result of improved bonding and more even growth of the first ALD-grown layers on the polymeric substrate surface. The OTR of the plain B(PE) decreased from 7900 to 5700 cm³/m²/10⁵ Pa/day and the WVTR from 7.0 to 6.2 g/m²/day with the corona treatment. When B(PE) was coated with an Al₂O₃ layer, the values did not drop significantly. The values were 6700 cm³/m²/10⁵ Pa/day in the case of OTR and 6.9 g/m²/day and in the case of WVTR. However, when these samples were corona-treated prior to ALD, the barrier level was improved and the OTR was 1400 cm³/m²/10⁵ Pa/day and the WVTR 6.1 g/m²/day. After the corona treatment, the standard deviations of the OTR and WVTR seemed to decrease in many cases, implying that the treatment would lead to more uniform barrier properties probably due to more uniform ALD-grown layers.

Corona treatment caused the surface of B1(PLA) to become more hydrophilic, decreasing the contact angle value from 71 to 62°. After seven days the influence was minor and the contact angle was measured at 67°. The change was minor for B1(PLA) probably due to polar groups already existing on the surface of PLA. The barrier properties of plain and Al₂O₃-coated substrates with and without corona pre-treatment are presented in Table 6.

Table 6. OTR and WVTR values of plain and ALD-Al₂O₃ coated (25–50 nm) B1(PLA) substrates with and without corona treatment.

	OTR (cm ³ /m ² /10 ⁵ Pa/day)		WVTR (g/m ² /day)	
Sample	Untreated	Corona treated	Untreated	Corona treated
B1(PLA)	420 ± 10	330 ± 1	65 ± 1.6	61 ± 0.4
B1(PLA) + 25 nm	20 ± 3	17 ± 5	1.4 ± 0.2	5.7 ± 3.8
B1(PLA) + 50 nm	60 ± 5	80 ± 50	1.8 ± 0.5	14 ± 5.9

The best OTR values were achieved with a 25-nm Al₂O₃ layer on top of a corona pre-treated substrate. The influence of corona treatment was minor on the barrier properties of B1(PLA), probably due to the minor increase in surface polarity of the pristine substrates. The initial Al₂O₃ layers and subsequent Al₂O₃ layers have different functions. While the first layers influence the adhesion, the further layers serve to increase the film's rigidity. No further improvement in barrier performance was achieved by a 50-nm Al₂O₃ layer, which may be due to the cracking behaviour of thick ALD films. The corona pre-treatment did not improve the WVTR value. The increased surface polarity may aid the adhesion of polar H₂O molecules to the surface and thus the permeation through the material decreasing water vapour barrier properties. On the other hand, a more uniform layer provides a better oxygen barrier.

6.4.2 Enhanced polymer crystallinity by thermal treatment

Thermal pre-treatment of polymeric materials prior to the ALD process could increase crystallinity, which could in turn have an effect on barrier properties by altering the surface chemistry and topography of the material. Here, B3(PLA) was used as the substrate material. Topography measurements by AFM indicated that thermal treatment caused the substrate surface to become smoother. The average roughness (R_a) values measured from 5*5 µm² images decreased from

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110 to 27 nm already with the shortest thermal treatment time (4 minutes). The R_a value was not significantly different with longer thermal treatments (9 or 16 minutes).

The effect of thermal treatment on B3(PLA) is presented in Figure 11 as phase AFM images. Surface roughness as such has probably little effect on barrier properties if this is insignificant compared to the overall thickness of the barrier layer. However, surface irregularities may affect the initial wetting of the polymer by liquids, and irregularities of specific size can cause condensation and cluster formation of gaseous permeants, which may affect the dynamics of mass transfer. The amount of spherulites increased with increased thermal treatment time. The shortest thermal treatment (4 minutes) had only a small impairing effect on the oxygen barrier properties of the plain B3(PLA) substrates. The increased crystallinity of treated for 9 and 16 minutes seemed to create discontinuation points between the spherulites, which were noticed to destroy the oxygen barrier properties. WAXS analysis revealed that the crystallinity of B3(PLA) grew with increasing treatment time.

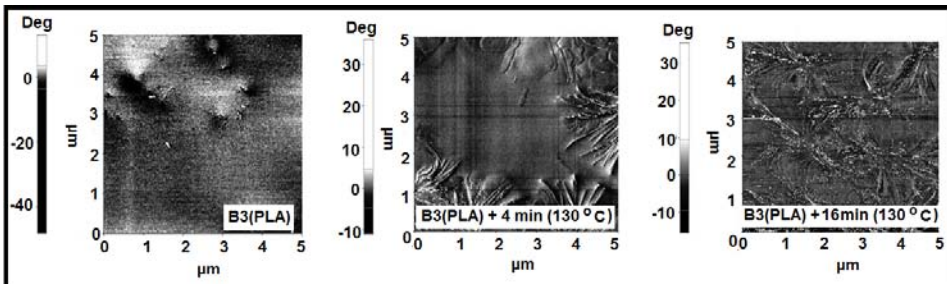


Figure 11. AFM phase images of plain B3(PLA) substrate and B3(PLA) after 4 and 16 minutes of thermal treatment for smoothened polymer surface.

Although the influence of thermal treatments on the morphology of the substrates was significant, the influence on improving barrier properties of the Al_2O_3 -coated samples was minor. The most significant improvement in OTR values was realized when the 4-minute thermally-treated sample was coated with a 25-nm ALD-grown Al_2O_3 film. The OTR value decreased from 650 to 40 $\text{cm}^3/\text{m}^2/10^5 \text{ Pa/day}$. The coating of 9- and 16-minute treated samples with the Al_2O_3 film did not improve the oxygen barrier properties. On the contrary to the OTR values, the WVTR value of plain B3(PLA) substrates was improved with all of the treatment times, and most with the 16-minute thermal treatment,

from 98 to 76 g/m²/day. The Al₂O₃ coating decreased the value to 11 g/m²/day. With 4- and 9-minute thermally-treated samples, the WVTR values were 88 and 78 g/m²/day prior to ALD, respectively. The WVTR values dropped to 3.0 and 3.2 g/m²/day, respectively, with the Al₂O₃ coating. The results indicated that the Al₂O₃ coating dominates water vapour barrier properties more than changes in crystallinity of the polymeric substrates. In addition, the oxygen barrier seems to be more sensitive to resulting coating defects than water vapor barrier. The WVTR is affected by the overall properties of the barrier layers.

6.4.3 Epoxy-SG layer as a pre-barrier for Al₂O₃-coated biopolymeric substrates

Besides pre-treatments, the barrier properties of polymeric materials can be improved by pre-blocking the biggest pinholes in the polymeric material by applying a coarser coating method than ALD. Despite the promising results achieved by coating the biopolymeric materials with the ALD-grown Al₂O₃ layer, further improvements are still desired. A pre-barrier layer fabricated using a coarser deposition method could close the larger pinholes on the surface of a porous substrate, making it denser and thus a more favourable surface on which to grow Al₂O₃ barrier layers.

The effect of a sol-gel (SG) coating as an intermediate layer between the substrate and the ALD-Al₂O₃ coating was studied using B2(PLA) as a substrate. Figure 12 shows the surfaces of plain, epoxy-SG-coated and epoxy-SG+Al₂O₃-coated B2(PLA) substrates. The observed average roughness (R_a) values are also given. As can be seen in Figure 12, the epoxy-SG coating decreases the R_a value making the surface of the substrate smoother, while an Al₂O₃ coating on epoxy-SG-coated B2(PLA) makes the surface smoother still. The total decrease in R_a was from 54 to 15 nm.

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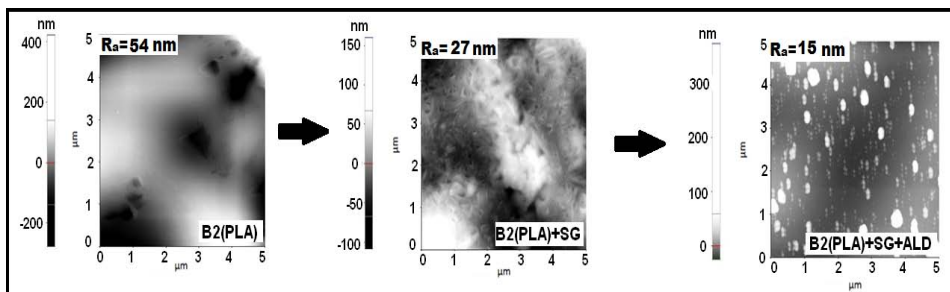


Figure 12. AFM surface images of plain B2(PLA) with SG coating and with a multilayer structure consisting of SG and Al_2O_3 layers.

The contact angle (CA) and surface energy (γ_s) values for plain, epoxy-SG-coated and epoxy-SG-+ Al_2O_3 -coated B2(PLA) samples are presented in Table 7 together with the barrier results. The intermediate layer decreases the CA value, indicating a more hydrophilic surface. The CA value drops even further with an additional Al_2O_3 coating. The barrier results show a moderate positive effect of epoxy-SG coating on barrier properties. Only after the SG-coated B2(PLA) was further coated with Al_2O_3 were the considerably low OTR and WVTR values of $2 \text{ cm}^3/\text{m}^2/10^5 \text{ Pa/day}$ and $2 \text{ g/m}^2/\text{day}$, respectively, attained. Most importantly, these values are lower than those achieved for B2(PLA) with the ALD- Al_2O_3 coating only, i.e. $6 \text{ cm}^3/\text{m}^2/10^5 \text{ Pa/day}$ and $3 \text{ g/m}^2/\text{day}$, respectively. Table 7 presents the impact of epoxy-SG coating on the CA and on the surface energy values, showing also the OTR and WVTR values. The total surface energy value (γ_s) is the sum of the dispersive (γ^d) and polar (γ^p) components.

Table 7. Contact angle and surface energy values together with the OTR and WVTR values, showing the impact of epoxy-SG pre-coating.

Sample	CA(°)	$\gamma_s (\gamma^p)$ (mNm^{-1})	OTR ($\text{cm}^3/\text{m}^2/10^5$ Pa/day)	WVTR ($\text{g/m}^2/\text{day}$)
B2(PLA)	71 ± 2	45.6 (7.4)	400 ± 9	75 ± 2
B2(PLA) + epoxy-SG	58 ± 2	53.8 (13.2)	310 ± 2	44 ± 2
B2(PLA) + epoxy-SG + 25 nm Al_2O_3	52 ± 1	54.9 (18.0)	2 ± 1	2 ± 1

6.4.4 Polyelectrolyte multilayer film as a pre-coating for Al_2O_3 -coated biopolymeric substrates

In addition to pre-blocking the biggest pinholes prior to the ALD process, pre-coatings can also be utilized to alter the surface topography. Here, the effect of pre-coating the polymer film with a PEM film to improve barrier properties was investigated by using PLA1 as a substrate material. The PEM film was made by alternating depositions of sodium alginate (ALG) (M_v 280 000 g/mol) and chitosan (CHI) (M_v 170 000 g/mol), leaving CHI as the outermost layer. The PEM-coated PLA1 film was further coated with a 25-nm-thick ALD-grown Al_2O_3 layer. Figure 13 presents the targeted three-layer structure.

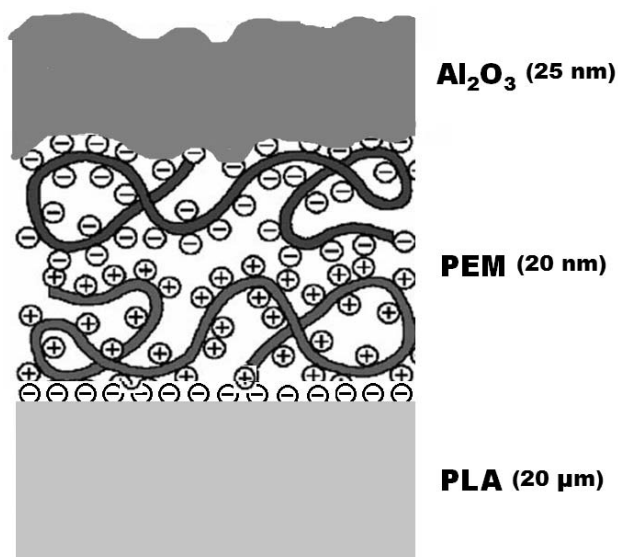


Figure 13. Schematic illustration of the multilayer structure of PEM- and Al_2O_3 -coated film, modified from that of Decher [120].

The average thickness of the film formed from ALG and CHI was 20 nm. The PEM coating alone did not improve the water vapour barrier properties of the substrate. In contrast, the WVTR value was increased from 53 to 106 $\text{g/m}^2/\text{day}$ after PEM coating. This is apparently due to the dipping process in the LbL method, which causes the hygroscopic biopolymers to swell in water solutions. However, after the Al_2O_3 coating had been applied on PEM-coated PLA1, the WVTR was improved to 25 $\text{g/m}^2/\text{day}$. When applying only the Al_2O_3 coating,

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the WVTR was 33 g/m²/day. PEM coating combined with Al₂O₃ coating was found to be a suitable and cost-efficient means of producing bio-based water vapour barrier coatings. The WVTR and contact angle values of variously-coated PLA1 films are presented in Table 8.

Table 8. Water vapour transmission rate (WVTR) and contact angle (CA) values for plain and variously coated PLA1 samples.

Sample	WVTR (g/m ² /day)	CA (°)
PLA	53 ± 4	73 ± 2
PLA + PEM	106 ± 7	76 ± 4
PLA + 25 nm Al ₂ O ₃	33 ± 6	48 ± 1
PLA + PEM + 25 nm Al ₂ O ₃	25 ± 9	98 ± 4

From Table 8, the water vapour transmission rates seem to correlate with the wettability properties of the Al₂O₃-coated samples such that the larger the CA, the lower the WVTR value. Polar H₂O molecules are apparently less readily adsorbed on the less polar surface. The contact angle value of the plain PLA1 film was 73°. The PEM coating alone did not change the contact angle value considerably. However, when the PEM-coated PLA1 film was further coated with an Al₂O₃ layer, the contact angle value increased to 98° thus making the surface more hydrophobic. Conversely, when the PLA1 film was coated only with the Al₂O₃ layer, the contact angle value was found to decrease to 48°, making the surface rather more hydrophilic. This result was expected, due to the intrinsically hydrophilic nature of Al₂O₃ surfaces [144].

Based on the above (Table 8), the PEM intermediate layer seems to influence the hydrophobicity of the Al₂O₃ surface. The precise reason for this remains to be determined by future studies. However, parallel behaviour (i.e. a CA value of 128°) was recently observed with a thermally-grown Al₂O₃ coating with a relatively rough surface [145]. It is known that certain special surface topologies can even produce superhydrophobic states on intrinsically hydrophilic surfaces [146]. The LbL dipping process may alter the surface of the PLA1 film and increase its roughness.

Figure 14 shows some SEM images of the plain and variously coated PLA1 films. The plain PLA1 substrate appears to be smooth with small patterns caused by the sputtered Pt. Nonconductive samples tend to charge when scanned by the electron beam causing possible scanning faults. They are therefore usually

sputtered with a thin coating of electrically-conducting material, such as Pt. The PEM-film-coated PLA1 substrate seems to have nanopores throughout the film. After further coating with a 25-nm-thick Al_2O_3 layer the surface seems to be uniformly coated with the Al_2O_3 layer.

As can be seen, the PLA1 film is a highly smooth substrate, presumably due to the commercial production method of the film. Some surface patterning can be observed, deriving from the sputtered Pt. Once the PLA1 film is coated with a PEM film, a surface structure with small pores (10–30 nm in diameter) appears on the entire surface of the film. After subsequent deposition of the 25-nm-thick Al_2O_3 layer, the nanostructured surface appears to be uniformly coated with Al_2O_3 , such that the smallest pores are filled, yet the surface still presents some surface structure.

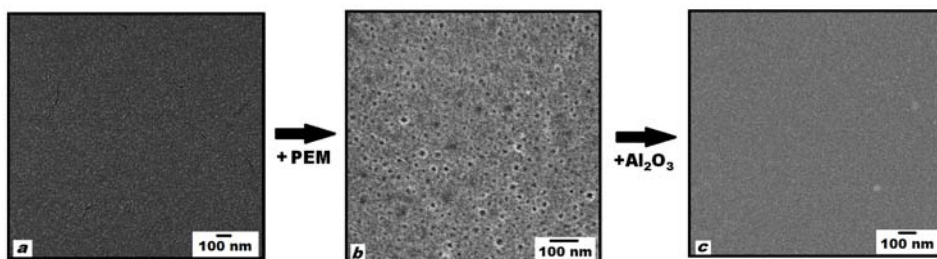


Figure 14. SEM images for plain (a) and variously coated PLA1 films (b–c).

7. Conclusions

The objective of the present work was to investigate the suitability of ALD-grown Al_2O_3 layers as barrier coatings for bio-based packaging materials. The focus was to determine whether ALD is the most feasible thin-film deposition technique for the production of high-quality barrier coatings on polymeric materials. Thereafter, the task was to clarify whether the ALD process could be performed in the temperature range of 80–130 °C on biopolymeric materials known to be temperature-sensitive. The ALD process parameters (oxygen source, deposition temperature, and film thickness) were optimized, which enabled the investigation of the oxygen and water vapour barrier properties of thin ALD-grown Al_2O_3 coatings on polymer films and polymer-coated papers and boards. An additional objective of this study was to improve the barrier properties of ALD-coated materials by employing treatments and coatings on the substrates prior to the ALD process.

By utilizing ALD-grown Al_2O_3 coatings with thicknesses of 10–50 nm, the oxygen and water vapour barrier properties of biopolymeric materials could be significantly improved. The barrier ability was achieved without the use of conventional aluminium film, thus achieving total biodegradability due to the thinness of the Al_2O_3 layer. The ALD-grown Al_2O_3 layer required to provide sufficient barrier properties is so thin that it should not affect the biodegradability of the substrate material.

The developed coatings with excellent gas and water vapour permeation resistance offer a new means of manufacturing biodegradable, thin, light and air-tight packaging materials. The oxygen and water vapour barrier levels achieved here with the Al_2O_3 coatings grown onto biopolymeric materials reached the level required in commercial packaging applications for dry food and pharmaceuticals. Other thin film methods can also produce thin Al_2O_3 coatings; however, their gas and water vapour permeability is higher and the material is

stiffer and breaks easily. With these competing methods, comparable permeation resistance is possible only if thicker films are used.

Although a number of additional substrate pre-treatments and pre-coatings can be employed prior to the ALD process, the overall improvement in barrier properties gained by ALD-grown Al_2O_3 layers seems sufficient. However, such pre-treatments and pre-barrier coatings could make the materials and processes in some cases more cost-efficient at the industrial scale.

With some polymeric substrates, a deposition temperature of even 80 °C may be too high to achieve the most desirable barrier properties. This highlights the need for future research to develop efficient ALD processes at temperatures as low as 50 °C. In addition to corona and thermal pre-treatments, other pre-treatments such as plasma and flame spray treatments need to be investigated in future to clarify the overall potential of various pre-treatments to improve the barrier properties. As regards the characterization of Al_2O_3 coatings on biopolymers, cross-cut imaging of 25 nm thick or thinner Al_2O_3 layers has proven challenging due to the sensitive nature of the substrates. These imaging difficulties need to be overcome in order to be able to truly determine Al_2O_3 layer growth with respect to different substrate types.

The fabrication of nanolaminates wholly from several metal oxides or by utilizing molecular layer deposition (MLD) at low temperature for barrier purposes requires investigation in future. The resulting novel structures have the potential to provide improved flexibility as well as good barrier properties combined. By using the ALD process, different functions can be integrated in the packaging material, such as antimicrobial properties. As regards production of packages, the behaviour of Al_2O_3 layers during processes, such as sealing, greasing and laminating, is another significant area for future research.

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Terhi Hirvikorpi

Thin Al₂O₃ barrier coatings grown on bio-based packaging materials by atomic layer deposition

Growing environmental concerns related to the use of non-biodegradable polymers in the packaging industry have led to the need for new materials. Currently, these conventional polymers are widely used due to their relatively low cost and high performance. Bio-degradable plastics and fibre-based materials have been proposed as a solution to the waste problems related to these synthetic polymers. Fibre-based packaging materials have many advantages over their non-biodegradable competitors, such as stiffness vs. weight ratio and recyclability. However, poor barrier properties and sensitivity to moisture are the main challenges restricting their use. Application of a thin coating layer is one way to overcome these problems and to improve the barrier properties of such materials.

Atomic Layer Deposition (ALD) is a well suited technique for depositing thin inorganic coatings onto temperature-sensitive materials such as polymer-coated board and paper and polymer films. Thin and highly uniform Al₂O₃ coatings have been deposited at relatively low temperatures of 80, 100 and 130 °C onto various bio-based polymeric materials employing the ALD technique. The work demonstrates that a 25-nm-thick ALD-grown Al₂O₃ coating significantly enhances the oxygen and water vapour barrier performance of these materials. Promising barrier properties were revealed for polylactide-coated board, hemicellulose-coated board as well as various biopolymer (polylactide, pectin and nanofibrillated cellulose) films after coating with a 25-nm-thick Al₂O₃ layer.

Extremely thin Al₂O₃ coatings can improve the properties of biopolymers, enabling the use of these renewable polymers in the production of high-performance materials for demanding food and pharmaceutical packaging applications. The future roll-to-roll ALD technology for coating polymers with inorganic thin films will increase the industrial potential of these materials and could lead to further opportunities for their commercialization.

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Ohuet biopohjaisille pakkausmateriaaleille atomikerrosväskasvatetut Al₂O₃-barrierpinnoitteet

Pakkausteollisuuden tietoisuus synteettisten biohajoamattomien muovien ympäristöhaitoista on lisännyt tarvetta ekologisemmille biopohjaisille pakkausratkaisuille. Nykyisin näitä synteettisiä polymeerejä käytetään useissa pakkauksissa, koska ne ovat halpoja ja ominaisuuksiltaan hyviä. Biohajoavia muovi- ja kuitupohjaisia materiaaleja pidetään ratkaisuna öljypohjaisten synteettisten muovien aiheuttamalle jäteongelmalle. Kuitupohjaisilla pakkausmateriaaleilla on monia hyviä ominaisuuksia verrattuna niiden biohajoamattomiin kilpailijoihin, kuten painoon suhteutettu kestävyys ja kierrätettävyys. Niiden heikkoutena on kuitenkin huono kosteuden sietokyky sekä heikko vesihöyryn läpäisyn estokyky, jotka estävät tuotteiden laajamittaisemman käytön. Materiaalien läpäisyntoa voidaan parantaa sopivilla pinnoituksilla.

Työssä kasvatettiin ohuita Al₂O₃-kalvoja suhteellisen alhaisessa lämpötilassa 80, 100 ja 130 °C:ssa ALD-tekniikalla monenlaisille biopohjaisille polymeeri-substraateille. Hyvin ohuet (25 nm) ALD-tekniikalla valmistetut Al₂O₃-pinnoitteet saavat aikaan huomattavan parannuksen biopohjaisen pakkausmateriaalin hapen- ja vesihöyryn läpäisyn esto-ominaisuuksissa. Polylaktidilla ja hemiselluloosalla päällystetyt kartonkien sekä polylaktidista, pektiinistä ja nanoselluloosasta valmistettujen kalvojen huomattiin olevan lupaavia barriereja sen jälkeen, kun ne on päällystetty 25 nm:n paksuisella Al₂O₃-kerroksella.

Nämä hyvin ohuet pinnoitteet saavat aikaan niin suuren parannuksen barrier-ominaisuuksissa, että biopolymeerien käyttö vaativissakin pakkaussovelluksissa, kuten elintarvike- ja lääkepakauksissa, mahdollistuu. ALD-tekniikan kehitys kohti rullalta-rullalle-prosessia mahdollistaa epäorgaanisten pinnoitteiden valmistamisen teollisessa mittakaavassa, mikä on elintärkeää tässä työssä esiteltujen uusien pakkausmateriaalien kaupallistumiselle.

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Growing environmental concerns related to the use of synthetic, non-biodegradable polymers in packaging industry has led to the need for new, especially bio-based materials. Currently petroleum-based synthetic polymers are widely used due to their relatively low cost and high performance. Bio-based packaging materials can have many advantages over their non-biodegradable competitors, such as stiffness vs. weight ratio and biodegradability. However, poor barrier properties and sensitivity towards moisture are the main challenges for their use.

Atomic Layer Deposition (ALD) is a feasible technique to deposit thin aluminium oxide (Al_2O_3) coatings onto temperature-sensitive bio-based materials. Such coatings enhance significantly the barrier performance towards oxygen and water vapor. Even extremely thin (25 nm) Al_2O_3 coatings can provide improvement enabling the use of bio-based materials in fabrication of high-performance materials for demanding food and pharmaceutical packaging applications. The future use of roll-to-roll ALD process to coat biopolymers with ALD-grown inorganic thin-films will increase the industrial potential of these materials and is essential for the commercialization.